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ON THE ABSORPTION OF HYDROGEN BY SODIUM-POTASSIUM ELECTRODES.

By R. C. Gowdy.

MEY[1] has shown that the liquid alloy of sodium and potassium, when used as a cathode for the glow discharge, absorbs all except the inert gases. He found that with hydrogen and nitrogen the hydrides and nitrides of the metals were formed and that the rate of absorption was proportional to the current.

Skinner[2] and Cunningham[3] have experimented on the evolution of gas from various electrodes and have found that most metals liberate gas for a certain period at a rate equal to that defined by Faraday's law for electrolytic decomposition. Chrisler[4] has observed the electrolytic rate for the absorption of hydrogen by various anodes, among them, anodes composed of sodium-potassium alloy.

This alloy then presents the anomaly that it may absorb hydrogen when operated as cathode or as anode.

The object of the present experiments was to investigate the behavior of sodium-potassium electrodes in glow discharge in hydrogen.

Apparatus and Experimental Method.

Discharge tubes of the form shown in Fig. 1 were used.

The alloy was introduced into the bulb *B*, which was afterwards sealed off at *F*.

After evacuating the apparatus and washing out with dry hydrogen, the tube was tilted and the alloy allowed to run into the discharge tube. A trap, *D*, prevented specks of oxide from being carried over. A clean

[1] Mey, Annalen der Physik, 11, 1903.

[2] Skinner, Phys. Rev., XXI., p. 1 and p. 169. Phys. Zeit., 6, p. 610. Phil. Mag. (6), Vol. 12, p. 481.

[3] Cunningham, Phil. Mag. (6), IX., 1905, p. 193.

[4] Chrisler, Phys. Rev., XXIX., Nov., 1909.

surface could thus be obtained. A large glass spiral, later replaced by a mercury-sealed ground joint, provided the necessary flexible connection between the discharge tube and the pump and gauge. The auxiliary electrode, *E*, was used when a preliminary cleansing discharge was sent through the tube to free the upper electrode of gas.

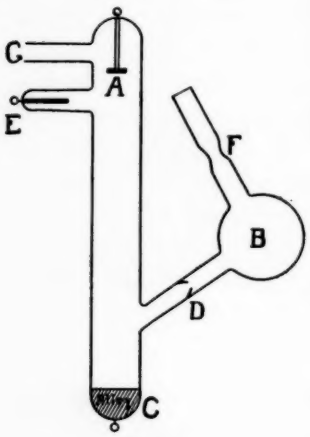

Fig. 1.

The absorption was determined by observing the change in pressure as indicated by a McLeod gauge. The apparatus was calibrated by admitting a known volume of gas and noting the change in gauge reading.

The rates of absorption were determined by plotting curves with pressures as ordinates and total duration of discharge as abscissæ, and determining the slopes of these curves at the required points.

The hydrogen used was produced by electrolysis of barium hydroxide and was carefully dried with sulphuric acid and phosphorus pentoxide.

Cathode Absorption.

Tables I. and II. give the initial rates of absorption of hydrogen by K-Na cathodes for various current strengths. The results in Table I. are for a cathode 30 mm. in diameter, those in Table II. for one of 16 mm. diameter.

Table I.

Diam. of Tube 30 Mm.	
Current in milli-amps.	Rate of absorption in mm.³ per Sec.
0.20	0.141
0.40	0.323
0.60	0.541
0.93	0.885
1.00	0.973
1.20	1.14
1.48	1.44
1.60	1.64
1.91	2.12
2.20	2.40
2.30	2.73
2.50	2.88
2.80	2.84
3.20	2.82
4.20	2.86
4.70	2.82

Table II.

Diam. of Tube 16 Mm.	
Current in milli-amps.	Rate of absorption in mm.³ per Sec.
0.20	0.21
0.44	0.33
0.48	0.38
0.64	0.45
0.70	0.68
1.10	0.59
2.00	0.50

These rates were determined by finding the slope of the pressure-time curve at the point where it meets the pressure axis and therefore represent the initial rates of absorption. When the surface is clean the rate of absorption is a maximum, but decreases rapidly as the film of hydride forms on the surface. The rate of absorption by a clean surface can not be found directly from the observations but must be determined by graphic extrapolation from the curves.

The film of hydride was decomposed and the surface cleaned before each set of observations, by running the alloy as anode at a pressure of about 0.03 mm.

The curves in Fig. 2 show graphically the results given in Tables I. and II.

The curves show that the rate of absorption increases a little more rapidly than the current up to a certain current strength, above which the rate of absorption is constant.

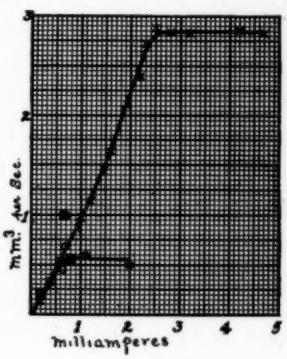

Fig. 2.

The total areas of the electrodes were in the proportion of about $3\frac{1}{2}$: 1, but the edge of the alloy for about 2 mm. in from the sides of the tube is practically inactive, as shown by the fact the surface shows little or no discoloration in this region. The active electrode areas were in the ratio of about 4.7 : 1. This is very nearly the ratio of the current strengths at which the rates of absorption become constant, which indicates that this takes place at a certain current density,—about 0.5 milliamps. per cm.^{2}

The rate of absorption below this current density is nearly ten times the electrolytic rate.

Two experiments were also tried to determine the effect of the temperature of the cathode on the rate of absorption.

The lower part of the tube containing the alloy was immersed in oil and heated to 140° C. A current of 0.66 milliamps. was used and the rate of absorption was found to be 1.0 mm.^{3} per sec. This is shown on the curve in Fig. 2 by a point marked with a square, and is much greater than the rate at room temperature for the same current. The cathode was frozen with solid carbon dioxide and probably reached a temperature of at least —20° C. The rate of absorption at 0.8 milliamps. was found to be 0.58 mm.^{3} per sec. This is also shown on the curve in Fig. 2 and lies considerably below the curve taken at room temperature.

ANODE EVOLUTION.

At pressures of one to two millimeters the K-Na anode absorbs hydrogen and at low pressures evolves it. There must be some equilibrium pressure at which it neither evolves nor absorbs. A number of experiments were made to determine this pressure, but while it is sharply defined in any one experiment, it varies from time to time, being dependent on the history of the tube,—primarily on the quantity of hydride available for decomposition: the more hydride present the higher will be the equilibrium pressure. It was found generally to lie below 0.160 mm., this pressure being obtained with a thick coating of hydride. A thin, almost imperceptible coating gave an equilibrium pressure of about 0.06 mm. By continued discharge the supply of hydride may be so far diminished that the equilibrium pressure may be reduced to one or two hundredths of a millimeter. It could probably be reduced still further were it not for the fact that the tube, when operated with an induction coil, tends to reverse at low pressures, becoming in fact, a more efficient rectifier than the " valve " tube with which it was connected.

Until a method was found to account for the quantity of hydride present, measurements of the relative variation of the equilibrium pressure with the current could not be made.

It seemed probable that the decomposition of the hydride was due to the impact of the cathode rays. To test this hypothesis an electromagnet was so placed that a field could be made to pass transversely through the tube a few centimeters above the surface of the alloy. Equilibrium pressure was established at 0.145 mm. with the magnetic field off. On applying the field, the discharge current being kept constant, the pressure in the tube decreased, finally reaching a steady value at 0.053 mm. This could not have been due to any effect arising from the deflection of the rays against the side of the tube, for when the field was reversed, projecting the rays against the opposite wall, the presure remaining unaltered. On removing the magnetic field the pressure rose to its original value.

That the decomposition of the hydride is due to the impact of the cathode rays, is indicated by the following experiment. A thin film of hydride was formed on the surface of the alloy, which was then insulated. A discharge was then passed from the auxiliary electrode, *E*, as anode, to the electrode *A* as cathode. A strong magnetic field traversed the tube below *E*, preventing the cathode rays from reaching the alloy. The pressure was so low that the tube glowed with a bright green fluorescence. The discharge was passed for five minutes with no change in the appearance of the tube. On removing the field and allowing the cathode rays

to strike the alloy, the pressure rose rapidly, the green fluorescence disappearing in a few seconds. A second application of the field produced no further change in pressure.

The gas liberated by the anode was repeatedly tested spectroscopically; only hydrogen was found.

We have now a means of arriving at some more definite results concerning the equilibrium pressure. By applying the magnetic field during the discharge the pressure may be reduced below the normal equilibrium point without removing hydrogen from the tube, and experiments on the rate of evolution and the equilibrium pressure repeated as often as desired with the assurance that at a given pressure there is always the same quantity of hydride present.

An induction coil was used to supply the current, since at low pressures sufficient potential could not be obtained from the batteries. It was doubtful whether the shunted galvanometer, calibrated on constant current, gave a proper indication of the average current from the coil. A small silver voltmeter was placed in series with the tube and a current of one milliampere, as indicated by the galvanometer, was passed for one hour. The deposit of silver weighed 4 mg., indicating a current of 0.99 millimaps. and showing that the average current was registered with sufficient accuracy by the galvanometer.

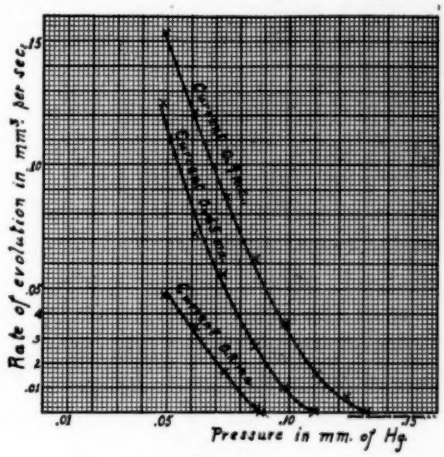

Fig. 3.

TABLE III.

Anode Evolution. Diam. of tube 30 mm.

Current = 0.9 m. amp.		Current = 0.45 m. amp.		Current = 0.20 m. amp.	
Pressure in Mm. of Hg.	Rate of Evolution in Mm.³ per Sec.	Pressure in Mm. of Hg.	Rate of Evolution in Mm.³ per Sec.	Pressure in Mm. of Hg.	Rate of Evolution in Mm.³ per Sec.
0.049	0.153	0.048	0.085	0.049	0.048
0.061	0.121	0.061	0.072	0.062	0.035
0.074	0.087	0.073	0.056	0.074	0.017
0.086	0.062	0.086	0.027	0.087	0.002
0.098	0.036	0.097	0.010	0.088	0.000
0.111	0.016	0.110	0.000		
0.123	0.006				
0.131	0.000				

The rates of evolution at various pressures for given current strengths are given in Table III., and shown graphically in Fig. 3.

The equilibrium pressure and the rate of evolution at any given pressure both increase with the current.

DISCUSSION.

Direct electrical action is insufficient to explain the high rate of cathode absorption observed. We have seen that this rate is considerably affected by the temperature in a sense indicating that the absorption may be largely due to a heating effect.

We have observed that K-Na anodes absorb hydrogen at high pressures, evolve hydrogen at low pressures, if the hydrides are present on the surface, and that, under this condition also, there is an equilibrium pressure at which neither absorption nor evolution takes place. We have also shown that the hydrides are decomposed by the direct impact of the cathode rays.

Apparently these phenomena are due to the rise in temperature produced by the impact of the charged particles.

Sodium and potassium hydrides are both formed at a temperature of about 350° C. and it is probable that in both cases decomposition begins below 400° C.[1] The combination therefore takes place within relatively narrow limits of temperature.

In the foregoing experiments the average temperature of the alloy was rarely above 40° C. and it is therefore unlikely that the average temperature of the surface was sufficient to form the hydrides. The temperature at the point struck by a charged particle of relatively small velocity may, however, be very high and the average temperature of the neighboring molecules might easily be of the order of three or four hundred degrees. Dunoyer[2] has suggested that this local heating effect may be sufficient to expel electrons from the electrode and even to vaporize the metal. In fact a simple calculation shows that a charged particle falling through ten volts possesses sufficient energy to raise ten atoms of sodium through 400° C. of temperature. We may therefore assume that at the point of impact the temperature is usually above the decomposition temperature and that only in a given zone surrounding this center the conditions exist favorable to the formation of the hydride. Thus at a given instant there is a given fraction of the surface of the electrode active is forming the hydride. When the charged particles fall so close together that the zones of favorable temperature begin to overlap, the active fraction of the surface will not be increased by further increase in the density of the

[1] Moissan, Compt. Rend., 134, p. 18 and p. 71, 1902.

[2] Dunoyer, "Sur la formation des rayons cathodiques," Le Radium, VII., Oct., 1910.

impinging particles. This may be the explanation of the maximum rate of absorption attained at a current density of 0.5 milliamps. per cm.[2] On this theory we should expect it to be possible to increase the area where dissociation is being produced until it would exceed the area where the hydride is being formed, *i. e.*, with a sufficiently strong discharge, the cathode, if coated with hydride, could be made to liberate hydrogen. This fact has been observed by Chrisler[1] who used a strong discharge in helium as a means of cleansing sodium cathodes, in the same manner that the writer used the anode discharge in hydrogen at low pressure to produce the dissociation of the hydrides. In the case mentioned the decomposition taking place at the hot center is in no way affected by the presence of the helium, while the chances of combination taking place in the zones where the temperature is favorable are greatly diminished, owing to the presence of the inactive gas; a resultant evolution of hydrogen therefore takes place.

The behavior of the K-Na anode is readily explained in the same manner. In fact, from the point of view of heating effects, there is little difference between the two cases, since the energies of the positive and negative particles are comparable in magnitude. It is necessary however to remark on certain differences in the conditions in the two sets of experiments:

1. Much higher potentials were used in the experiments on anode evolution,—due both to the lower pressure and to the valve action of the tube. There was therefore greater heating effect at the surface of the metal.

2. There was much less hydrogen in the neighborhood of the alloy when it was operated as anode,—due to the reduced pressure and to the fact that the hydrogen tends to accumulate near the cathode.

The existence of an equilibrium pressure may be explained as follows; Suppose that at a given pressure and current density, combination and decomposition are taking place at the same rate, due to an effective equality between the portions of the surface that are at a temperature favorable to the formation of the hydride and those that are too hot. If the pressure be raised the velocity of the particles is reduced and the heating effects lessened. There will therefore be a decrease in decomposition and a resultant absorption will take place, reducing the pressure until equilibrium is again established. If the pressure be reduced, the velocity of the particles is increased, the decomposition overbalances the absorption and the pressure is again raised to an equilibrium value.

The equilibrium pressure must also depend on the quantity of hydride

[1] Chrisler, loc. cit.

present. The less hydride, the less chance there is for decomposition and the more for combination. To bring about a balance between the two will require an increased area of high temperature, necessitating higher velocity of the impinging particles and consequently, reduced pressure.

The rise of equilibrium pressure with the current may be explained very simply if it be remembered that at equilibrium the areas of formation and decomposition must be effectively equal. If by increasing the current we increase the number of centers of dissociation there will be a resultant liberation of hydrogen which will continue until the increase in pressure diminishes the velocity of the particles sufficiently for equality to be again established.

The curve, Fig. 2, shows that the cathode absorption increases more rapidly than the current. This is what would be expected considering that, under the conditions of the experiment, an increase in current meant an increase both in the number of particles and in their velocity.

SUMMARY.

1. The rate of absorption of hydrogen by K-Na has been measured for various currents. At current densities less than 0.5 milliamps. per cm.^{2} the rate of absorption is approximately ten times that at which hydrogen is liberated by electrolysis with an equal current. With greater current densities the rate of absorption is constant. The rate of absorption increases with the temperature of the cathode.

2. An " equilibrium " pressure has been found at which K-Na anodes neither absorb nor evolve gas. This equilibrium pressure depends on the current and on the quantity of hydride on the surface of the alloy.

3. The rate of evolution by anodes below equilibrium pressure has been measured.

4. It has been shown that sodium and potassium hydrides are decomposed by the cathode rays.

The cathode absorption and anode evolution are regarded as being due to the formation or decomposition of the hydrides by the local heating effects of the impinging charged particles, according as the temperature is favorable to one or the other of these processes.

These experiments were carried on in part at the Cavendish Laboratory and the writer wishes in conclusion to tender his sincere thanks and appreciation to Professor Sir J. J. Thomson for his interest and helpful suggestions during the course of the work, and for his kindness in putting the facilities of the laboratory at the writer's disposal.

UNIVERSITY OF CINCINNATI,
DEPARTMENT OF PHYSICS,
July, 1914.

THE RELATION BETWEEN ALPHA-RAY ACTIVITIES AND RANGES IN THE ACTINIUM SERIES, WITH NOTES ON THE PERIOD AND RANGE OF RADIOACTINIUM

BY HERBERT N. MCCOY AND EDWIN D. LEMAN.

IT now seems well established that the number of ions, and therefore the ionization current in air due to a single particle of range R is very closely proportional to $R^{\frac{2}{3}}$.[1] In a recent paper,[2] it has been shown that the activity of each α-ray product of the thorium series is proportional to the $2/3$ power of its range, account being taken of the fact that ThC is complex. The activity of ThC found was in excellent agreement with that calculated for a multiple disintegration in which C_1 furnished 65 per cent. and C_2 35 per cent. as many α particles per second as the equilibrium amount of each of the other products of the thorium series, these being the percentages found in other ways by Marsden and Barratt[3] and Barratt.[4] The only discrepancy which appeared in the course of the work on thorium was traced to a large error in the accepted value for the range of ThX. But after the true range of ThX had been found, there was very good agreement between the observed activities and those calculated from the ranges of the various products. This led to the conclusion that there were no other α-ray products in that series than those already known; and that in each change, excepting that of the ThC, a single α particle is expelled from each exploding atom, while in the case of ThC the conclusions of Marsden and Barratt were fully confirmed.

In the present paper we wish to report the results of an analogous study of the actinium series, for which Table I. gives the latest available data.

We have prepared radioactinium (Rn) free from actinium itself as well as from actinium X, and subsequent products and measured its increase of alpha-ray activity with time, due to formation of AcX and its products. If f_1 is the fraction of the original Rn left after an interval of t days and f_2 is the fraction for AcX, unit amount being the equilibrium

[1] Geiger, Proc. Roy. Soc., *A*, *82*, 486 (1909). Taylor, Phil. Mag., *21*, 371 (1911). McCoy, PHYS. REV., *1*, 393 (1913).

[2] McCoy and Viol, Phil. Mag., *25*, 333 (1913).

[3] Proc. Lond. Phys. Soc., *24*, 50 (1912).

[4] Le Rad., *9*, 81 (1912).

quantity corresponding to the initial amount of Rn; then the activity, A, at time t, resulting from unit initial quantity of Rn is given by the equation:

$$A = f_1 + f_2 x, \qquad (1)$$

where x is the alpha-ray activity of the equilibrium quantity of AcX plus products for unit quantity of Rn. Strictly speaking, for intervals

TABLE I.

The Actinium Series.

	Symbols.	Periods.	Rays.	Ranges, Cm.
Actinium	Ac	?	—	—
Radioactinium	Rn	18.88 days[1]	$\alpha+\beta$	4.40[3]
Actinium X	AcX	11.35 days[2]	α	4.40
Emanation	Em	3.9 sec.	α	5.70
Actinium *A*	*A*	0.002 sec.	α	6.50
Actinium *B*	*B*	36 min.	β	—
Actinium *C*	*C*	2.1 min.	α	5.40
Actinium *D*	*D*	4.71 min.	$\beta+\gamma$	—

less than 3 or 4 days one should take into account the fact that the products of AcX are not in equilibrium with the latter; practically, however, for longer intervals, the simple equation (1) is entirely sufficient. If λ_1 and λ_2 are the decay constants of Rn and AcX respectively, then $f_1 = e^{-\lambda_1 t}$ and

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}).$$

The periods being 18.8 days and 11.35 days respectively, $\lambda_1 = 0.0369$ and $\lambda_2 = 0.0611$.

The actinium used in this work had been found to be free from all but negligible traces of radium and thorium and their active products.[4] It contained, however, an appreciable amount of ionium. To the solution of the actinium bearing material in dilute hydrochloric acid we added a few mg. of thorium nitrate and then precipitated the latter with hydrogen peroxide. The filtrate contained all the actinium and was apparently free from Rn and Io; but to be certain that no trace of the latter remained

[1] This paper.

[2] McCoy and Leman, Phys. Zeit., *14*, 1280 (1913). Hahn and Rothenbach found 11.6 days; Phys. Zeit., *14*, 409 (1913). The previously accepted periods of radioactinium and actinium X were 19.5 days and 10.2 days respectively.

[3] The range of radioactinium found by Geiger was 4.60 cm.; the value given above is that which we have found, as described in this paper.

[4] McCoy and Leman, loc. cit.

in the Ac, the treatment with Th and hydrogen peroxide was repeated three times. To the purified actinium solution 1 c.c. of 5 per cent. aluminium chloride solution was added and ammonia gas (free from carbon dioxide) passed in. The aluminium hydroxide was filtered out, dissolved in hydrochloric acid and precipitated with ammonia once more. The filtrate from the first aluminium precipitate contained two thirds of the AcX; that from the second the larger part of the balance; while 6 per cent. of the AcX remained in the third aluminium precipitate which contained practically all of the Ac. The precipitations with ammonia had freed the Ac from the minute amount of mesothorium introduced with the few milligrams of Th used. This Ac solution stood for several months during which time a large amount of Rn formed. The Rn was then separated from this solution, which had a volume of 5 c.c. by adding 3 drops of a 2 per cent. solution of thorium nitrate, which had just been freed from mesothorium, and precipitating the Th by hydrogen peroxide. The precipitate was filtered out, dissolved in dilute hydrochloric acid and potassium iodide, and precipitated by hydrogen peroxide four times more. The 10 c.c. of acid solution of the last Th precipitate which contained all the Rn but was entirely free from AcX and its products was treated with oxalic acid. The precipitate of 3 or 4 mg. of thorium oxalate contained all of the Rn. It was separated from the solution by a centrifuge, and washed thoroughly with water and then with alcohol. A small portion was then spread on a metal plate in an exceedingly thin film, the activity measurements of which are given in Table II.

TABLE II.

The Alpha-Ray Activity Curve of Radioactinium Initially Free from its Products. Film No. 4.

Interval in Days.	Activity.	x
0.000	1.000	
5.101	1.933	4.54
6.025	2.045	4.53
15.76	2.597	4.55
16.08	2.620	4.59
17.07	2.623	4.59
17.80	2.629	4.60
20.05	2.593	4.56
23.10	2.527	4.54
27.09	2.397	4.54
31.10	2.281	4.63
36.04	2.053	4.60
39.97	1.881	4.61
206.0	.007	4.573 mean

In the above table x is the activity of AcX + Em + A + B + C + D in terms of the activity of the equilibrium amount of Rn as unity.

The activity at the end of 206 days (Table II.) was found to be 0.007; of this 0.001 was calculated to be due to remaining Rn and products; the balance, 0.006, represents the constant activity of the minute amount of thorium present. The activities given in Table II. have been corrected for this constant thorium activity. The activity measurements were made in the alpha-ray electroscope previously described[1] having an ionization chamber 19.5 cm. square. The active films were placed 6.5 cm. below the charged electrode, thus allowing all rays to reach their full ranges. The activities of the films varied between half and one and one half that of the 35 sq. cm. standard film of uranium oxide. Sufficient potential, 500 to 600 volts, was used to insure practically complete saturation currents for the weak ionization measured.

Three other series of measurements like those represented by Table II. were made, with films made from two additional lots of radioactinium, each prepared and purified separately. The results for the four films are summarized in Table III.

TABLE III.

No. of Film.	No. of Observations.	x
1	18	4.59
2	14	4.57
3	15	4.55
4	12	4.57
		Mean 4.57

The value of x thus found is subject to a correction, which we estimate at 2.5 per cent., due to the effects of β rays, recoil, and loss of emanation. The corrected value is 4.68. By direct measurement we found that the β rays, largely from actinium D, increased the value of x 0.5 per cent. for the alpha-ray electroscope used in our measurements. To find the loss of activity due to recoil and loss of emanation we placed a brass plate charged to a negative potential of 110 volts one mm. above the radioactive film in a closed vessel and measured the activity which deposited on the plate during the first 16 days, following the preparation of the radioactinium film. Almost exactly half of the activity of the deposit was due to AcC; the balance decayed with the period of AcX, the presence of the latter substance being due to recoil. Assuming that all of the AcC lost by the film was deposited on the plate, the correction to x on this account would amount to 2 per cent. The correction for AcX, which is accompanied of course by Em and A, is also apparently 2 per cent., but should be taken somewhat less by reason of the probable

[1] McCoy and Ashman, Amer. Jour. Sci., *26*, 521 (1908).

extensive escape in the ionization chamber of the Em and A from the surface of the brass plate into the space above, where they would cause greater ionization than if they remained wholly on the plate. We estimate that the true correction should be 1.8 per cent. instead of 2 per cent. A further correction should be made because of the volatilization of Em and therefore of A from the principal film in the ionization chamber of the electroscope. From the amount of C in the active deposit, we estimate that 2 per cent. of the whole Em is present in gaseous form in the electroscope and that this would cause the value of x as found to be 0.8 per cent. too high. The combined effect of these corrections is $2 + 1.8 - 0.5 - 0.8 = 2.5$ per cent. Taking x uncorrected as 4.57, the corrected value becomes 4.68.

TABLE IV.

	Ranges at 15°.	$R^{\frac{3}{2}}$.	Percentage Activity.	
			Calculated.	Found.
Radioactinium	4.40	2.69	17.8	17.6
Actinium X	4.40	2.69	17.8	82.4
Emanation	5.70	3.19	21.1	
Actinium A	6.50	3.49	23.0	
Actinium C	5.40	3.08	20.3	
			100.0	

Table IV. shows the ranges, R, at 15° and 76 cm., $R^{\frac{3}{2}}$, and the percentage activity of each alpha-ray member of the series; these percentages are taken proportional to the corresponding values of $R^{\frac{3}{2}}$, it being assumed that the equilibrium amount of each member of the series produces the same number of alpha particles per second.[1] The values given in the last column of Table IV are those found by experiment: for radioactinium the "activity found" is $1/(1 + x) = 17.6$ per cent. of the whole. The value of $\Sigma R^{\frac{3}{2}}$ for AcX + Em + A + C divided by $R^{\frac{3}{2}}$ for Rn gives 4.63 which is therefore the theoretical value of x. The close agreement of this result with that found by experiment, 4.68, is further evidence, if such were necessary, that the roll of the alpha-ray members of the actinium series is now complete and that the constants given in Tables I. and IV. may be accepted with considerable confidence as being at least close approximates to the true values.

[1] While it is probable that AcC is complex, the number of α-particles of longer range than 5.4 cm. compared with those of this range is so small—0.15 per cent.—that we need not take them into account here. See Marsden and Perkins, Phil. Mag., *27*, 700 (1914).

Note One: The Period of Radioactinium.

Hahn's early work[1] on radioactinium indicated a period of 19.5 days. This value has been accepted during the past eight years and was thought to be confirmed by Rothenbach[2] during the past year, working under the direction of Professor Hahn. In determining the period of a radioactive substance, which produces products of considerably shorter life, it is usually practicable to consider that the rate of decay is exponential after a sufficient lapse of time. It was by this method of calculation that the period of radioactinium was determined by Hahn and by Rothenbach. However, in case the period of one or more of the products is of the same order of magnitude as that of the mother substance, this simple treatment of the problem is not accurate.

The familiar equation which we have used in the form

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

may be written

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} f_1[1 - e^{-(\lambda_2 - \lambda_1)t}] = \frac{p\lambda_2}{\lambda_2 - \lambda_1} f_1$$

if for $1 - e^{-(\lambda_2 - \lambda_1)t}$ we write p.

The equation

$$A = f_1 + f_2 x$$

then becomes

$$A = f_1 \left[1 + \frac{p\lambda_2 x}{\lambda_2 - \lambda_1}\right].$$

Now the limiting value of f_2 is given by

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} f_1$$

and to calculate the period of Rn by the simple exponential equation is to assume that f_2 has approached this limiting value sufficiently closely. But this is by no means the case, even after a much longer time than that over which Hahn's and Rothenbach's observations were carried. After 115 days the activity of a Rn film is about 6 per cent. less than it would be if the limiting ratio of AcX were present. Let us represent by A' the activity of the film if this limiting ratio of AcX (+ products) were present: then

$$A' = f_1 \left[1 + \frac{\lambda_2 x}{\lambda_2 - \lambda_1}\right]$$

[1] Phil. Mag., *12*, 244 (1906); *13*, 165 (1907).

[2] Dissertation, Berlin, 1913.

and

$$\frac{A'}{A} = \frac{\lambda_2 - \lambda_1 + \lambda_2 x}{\lambda_2 - \lambda_1 + p\lambda_2 x},$$

which expression we may call q, therefore $A' = qA$. It is obvious that the quantity A' will decrease with time strictly exponentially with the true period of Rn.

In order to find the period of Rn, we made a film from the larger part of the material used for the measurements recorded in Table II. This film had an initial activity nearly three times that of our uranium standard (about 35 sq. cm. of a thick film of U_3O_8). We made very careful measurements of its initial activity, extrapolating from the first measurements made 45 min. after the precipitation of the Rn with the thorium oxalate, to find the true activity at time zero. We allowed this film to decay for nearly four months and then made the measurements shown in Table V. between the 115th and 206th day, by which latter time the activity had fallen to 0.0469 of the uranium standard. Of this final activity we calculated that 0.0284 was due to the thorium present. We got this result by considering that of the activity observed at the 164th day, that due to Rn + products decayed exponentially with the period of 18.8 days, account being taken of the q factor. All of the observed activities given in Table IV. have been corrected for the constant activity of the thorium present. While a knowledge of the value of x is required for the calculation of q, any probable error in x is unimportant: thus, if x were 5.0 instead of 4.57, q would be changed by only 0.1 per cent. for the 115th day.

TABLE V.

Age of Film in Days.	Interval Since 115th Day.	Activity Found.	Activity Calculated.	q	Period of Radioactinium.
0.0	——	2.828			
115.1	0.00	0.4809	0.4804	1.060	——
117.1	2.02	0.4476	0.4473	1.058	18.94
127.9	12.02	0.3118	0.3129	1.045	18.68
132.0	16.91	0.2605	0.2630	1.040	18.60
139.1	24.00	0.2005	0.2032	1.033	18.56
145.9	30.82	0.1562	0.1592	1.028	18.59
152.9	37.80	0.1213	0.1238	1.024	18.67
160.0	44.89	0.0948	0.0954	1.020	18.84
164.1	49.01	0.0824	0.0823	1.018	18.97
206.0	90.87	0.0185	(0.0185)	1.007	(18.80)
			Mean Period found.....		18.74

From the consideration of all of our results on the change of activity of Rn films with time, we are led to conclude that the period of Rn is very

close to 18.8 days, although the results in Table V. lead to a mean of 18.74 days. We believe that better results for this constant would have been obtained if we had begun measurements before the activity of the film had become so small that the inevitable errors of measurement made appreciable errors in the period found. Using the value 18.8 days, we have calculated the activities to be expected from the activity, A_0, at time zero, by the strictly accurate equation

$$A = A_0(f_1 + f_2 x),$$

taking $A_0 = 2.828$ and $x = 4.57$. The results given in the column headed "Activity Calculated" were obtained in this way. It is seen that the agreement between these values and those found are quite as close as one could expect for films of such small activity. We have also made calculations of the activities at the various times upon the assumption that the period of Rn is 19.0 and 19.1 days. If the period of Rn is 19.1 days, the mean difference between the activities found and calculated is 5.9 per cent.; for a period of 19.0 days the difference is 3.7 per cent., while for a period of 18.8 days, the difference is only 0.8 per cent. It is therefore perfectly clear that the old value 19.5 days is far from the true value and can no longer be supported.

We find that the difference between our value for the period of radio-actinium and that of Hahn and Rothenbach is wholly due to the fact that in the latter case the formula used in the calculation was not sufficiently accurate. Our experimental results which are in satisfactory agreement with theirs, indicate also a period of 19.5 days, if we make the calculation by the simple exponential equation used by Hahn and Rothenbach. The latter's calculations were based on measurements made between the 115th and 174th day. Now a simple calculation will show that if the period as found by the simple exponential equation is 19.5 days for the interval between 120 and 139.5 days, then by use of the correct formula used by us, the same data show the true period to be 18.89 days.

Since the foregoing paragraphs were written we have completed four additional series of measurements of four new radio-actinium films and have obtained the results shown in Table VI.

TABLE VI.

Age of Film at First Measurement.	Age of Film at Last Measurement.	Number of Measurements.	Period.
60.1 days	109.2 days	11	18.88
60.1	118.0	12	18.88
104.0	120.0	7	18.75
92.2	119.2	6	18.88

The average difference between single results and the mean for the four series was 0.08 days. The low result, 18.75 days, for the third series was caused by three very low values found on successive measurements on the 9th, 12th and 14th days, viz: 18.56; 18.57; and 18.67. On both the 15th and 16th days, however, the measurements gave 18.84 days; and we are therefore inclined to think that these low results were caused by some undiscovered error in the activity measurement. If these low results are omitted from the mean, we obtain for this series 18.87 days, a value in good agreement with the means of the other three series.

These newer measurements indicate that the period of radioactinium is a little higher than 18.8 days, which value was used in finding the value $x = 4.68$. If, as is very probable, the period is 18.88 days, our experimental results give $x = 4.67$; the difference is not great and the lower value of x is in even closer agreement with the value calculated from the ranges, viz.: 4.63.

Note Two: *Determination of the Range of Radioactinium.*

The value found for the activity of the products of radioactinium compared with radioactinium itself led us to suspect either that the accepted range of radioactinium was too great or that of AcX too small. The values found by Geiger[1] for Rn and AcX at 15° and 760 mm. were 4.60 and 4.40 cm. respectively. Furthermore, by Geiger's law relating ranges and decay constants, the range of Rn should be less than that of AcX. As it was a comparatively easy matter to determine the range of Rn, we carried out this measurement, making use of a modification of Geiger's spherical flask apparatus. The flask, which was chosen from a large stock, was almost perfectly spherical, except in the region near the neck. Its internal radius was 6.7 cm.

The radiothorium was prepared by the same method as that used in preparing this substance for the activity measurements. A large quantity of actinium was used, and but one drop of a 0.4 per cent. thorium nitrate solution, = 0.1 mg. of ThO_2. The thorium was precipitated three times with hydrogen peroxide, and converted into oxalate, which was separated by means of a centrifuge and washed with dilute hydrochloric acid and finally with alcohol. A small portion of this oxalate was made into a very thin film, about 1 mm. in diameter on the center of the brass disc of the range apparatus. The range measurements were completed within two or three hours from the time of the oxalate precipitation; from which it follows that the maximum amount of AcX formed did not exceed 0.25 per cent. of the equilibrium amount. The

[1] Phil. Mag., *24*, 653 (1912).

temperature was read at frequent intervals during the measurement and always remained constant within one degree.

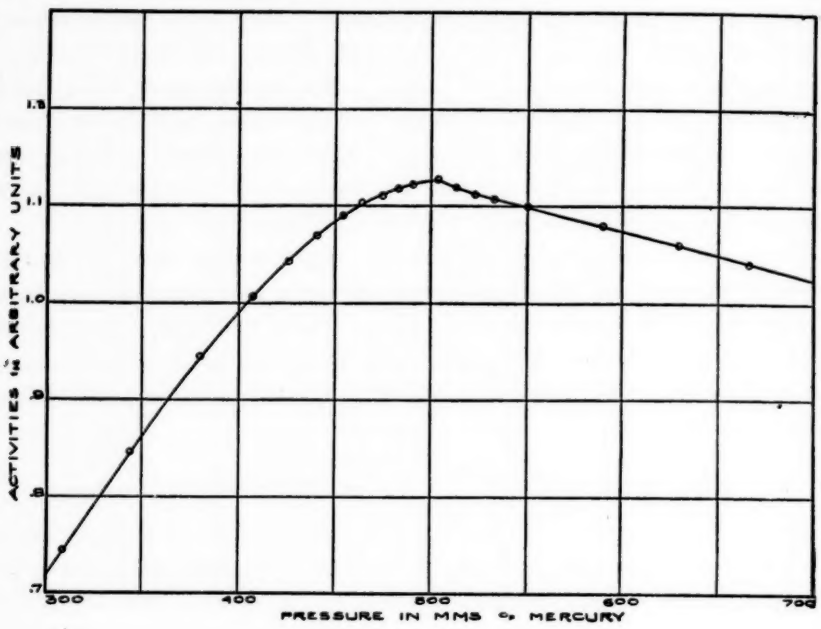

Fig. 1.

The results of one determination are shown graphically in Fig. 1, which is drawn to scale. The break comes at 504 mm. of mercury and as the temperature was 20°, this gives as the range of radioactinium 4.17 cm. at 760 mm. and 0°, or 4.40 cm. at 15°. We made two other determinations, each with separately prepared samples of radioactinium. One gave 4.38 cm., the other 4.43 cm. at 15°; the mean of the three results is 4.40 cm. for 15°. This is 0.20 cm. lower than Geiger found for radioactinium and is identical with Geiger's value of actinium *X*. The periods of radioactinium and actinium *X* being 18.8 and 11.35 days respectively, if the range of the former is 4.40 cm., that of the latter should by Geiger's law be 4.45 cm., which differs from the value found by Geiger by scarcely more than the experimental error of the measurements.

SUMMARY.

1. Methods are described for the chemical separation of radioactinium and also of actinium *X* from actinium and from one another and the preparation of each in radioactively pure form.

2. The period of radioactinium has been found to be 18.88 days instead of 19.5 days as accepted for many years. The old higher value resulted from an inaccurate method of calculation.

3. The period of actinium *X* has been found to be 11.35 days instead of 10.2 days. This result first published some months ago,[1] is in fair agreement with that found by Hahn and Rothenbach,[2] a few months earlier, viz.: 11.6 days.

4. The range of radioactinium at 15° and 76 cm. was found to be 4.40 cm. instead of 4.60 cm., as found by Geiger. The new value is in closer agreement than the old with Geiger's Law relating ranges and periods. This agreement is also improved by our results showing the period of radioactinium to be shorter and that of actinium *X* to be longer than the values formerly accepted. Complete agreement would result if the range of actinium *X* were 4.45 cm. instead of 4.40 cm. as given by Geiger.

5. Careful and extensive measurements of the change of the alpha ray activity of radioactinium with time has shown that the alpha activity of AcX + Em + A + C is 4.67 times that of the equilibrium amount of radioactinium alone. If in each atomic disintegration one and only one alpha ray is expelled, and if the ionization produced by any alpha ray is proportional to the 2/3 power of its range, we should expect this ratio to be 4.63. The good agreement between experiment and theory indicates the correctness of the latter. The important revised data for the actinium series are given in Tables I. and IV.

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UNIVERSITY OF CHICAGO,
June 20, 1914.

[1] Phys. Zeitschr., *14*, 1280 (1913).
[2] *Ibid.*, *14*, 409 (1913).

DETERMINATION OF THE VALUE OF "e," BY MILLIKAN'S METHOD, USING SOLID SPHERES.

BY JOHN YIUBONG LEE.

INTRODUCTION.

THE value of the elementary electric charge was very carefully determined by Millikan[1] by his well-known method. By varying the size of his drops and the pressure, he also obtained empirically a correction term for the law of Stokes on the rate of fall of spheres in viscous media. The following experiments were undertaken for the sake of seeing (1) whether solid spheres would give a value of e in any way different from that obtained with the liquid drops; and (2) whether the correction term to Stokes's law is the same for both solid and liquid drops.

The apparatus used was that employed by Millikan, with but slight modifications. The substance in liquid form is blown into very minute particles by means of a commerical atomizer (A, Fig. 1) into the dust free chamber D, where the drop solidifies and falls slowly to the top of the plate condenser near the bottom of the chamber. Some of the particles fall though the small holes (h) in the middle of the upper plate into the space between, where on account of the charge which they carry, they may be pulled upwards against the action of gravity by applying an electric field of sufficient strength and of the proper sign to the condenser plates.

The force acting on the particle while falling under the action of gravity is simply mg, while the force pulling it upwards is $Fe_n - mg$, where F is the field strength and e_n the charge on the particle. According to Stokes's law, the force acting on a solid sphere in a viscous medium is

$$x = 6\pi\eta a v, \tag{1}$$

where η is the viscosity of the medium, a, the radius of the particle, and v, the velocity of the fall. Now if v_1 represents the downward velocity and v_2 the upward velocity, we have

$$\frac{mg}{Fe_n - mg} = \frac{v_1}{v_2}. \tag{2}$$

[1] R. A. Millikan, PHYS. REV., N. S., Vol. II., p. 109–143, Aug., 1913.

Combining equations (1) and (2) and substituting for m, $(4/3)\pi a^3(\sigma-\rho)$, where σ is density of the particle, and ρ that of the medium, we obtain

$$e_n = \frac{4}{3}\left(\frac{9\eta}{2}\right)^{\frac{3}{2}}\left(\frac{1}{g(\sigma-\rho)}\right)^{\frac{1}{2}}\left(\frac{v_1+v_2}{F}\right)v_1^{\frac{1}{2}}. \qquad (3)$$

By repeatedly changing the charge on a given particle by allowing it to capture ions from the air, a series of values of v_2, and hence of e_n, may be obtained. The values of e_n for any given drop come out to be exact multiples of an elementary unit, e_1, which shows that the electric charge is atomic in structure. This value of e_1 is not the same, however, for small particles of varying sizes, a fact which led Millikan to the conclusion that Stokes's law breaks down when the dimensions of the particles are comparable with the mean free path of a gas molecule. Accordingly a corrected form of Stokes's law was set up; viz.

$$v_1 = \tfrac{2}{9}ga^2\frac{(\sigma-\rho)}{\eta}\left\{1+A\frac{l}{a}\right\}, \qquad (4)$$

in which A is a constant to be determined; l, the mean free path of a gas molecule, and a, the radius of the particle. From the variations of e_1 with the different values of l/a, A was shown to be determinable empirically by a graphical method.[1]

THE APPARATUS.

The arrangement of the apparatus is shown in Fig. 1. D is a heavy brass vessel about 30 cm. high, and 35 cm. in diameter. It has three glass windows (only two are shown in the figure), a and b, 180° apart, and c, 28° from b in the same horizontal plane with a and b. The light from an arc lamp A enters from the window a to illuminate the particles. An X-ray bulb is placed in front of the window b to ionize the air inside the chamber, and c is the observation window. The whole vessel is immersed in an oil bath, which is kept constant to within 0.1° C. for several hours before and during the observation. The heat rays from the arc are absorbed by means of a water cell 80 cm. long and a cupric chloride cell 4 cm. thick. The condenser plates are 22 cm. in diameter and are separated by three ebonite rods, 15.98 cm. in length. A thin ebonite strip entirely encircles the sides of the condenser, with the exception of three glass windows, which are directly opposite the three windows in the vessel D. The pressure is measured by a very carefully made barometer, which has been compared with a standard weather bureau barometer, and found to be correct. The atomizer is made entirely of glass,

[1] L. c.

and is cemented to one half of a union joint, by means of which it is attached to the vessel *D* immediately in front of the valve *W*. The space above the reservoir is connected to the vessel *D* also by means of a glass tube, so that the pressure at the nozzle and above the liquid in the reservoir is the same no matter what the pressure inside the vessel may be. This

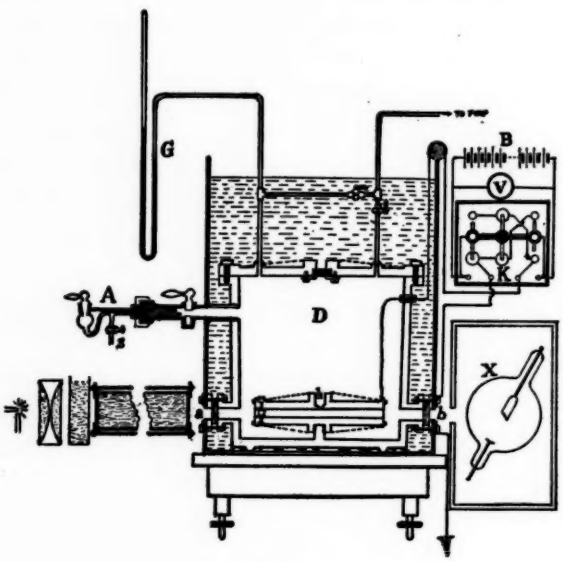

Fig. 1.

atomizer may be detached from the rest of the apparatus for cleaning without interfering with the vacuum in *D*, by simply closing the valve *W*. The electric field is produced by about 2,500 storage cells which gives a potential difference of about 5,000 volts. By means of a specially designed switch *k*, containing eight mercury cups and six movable contacts, the condenser may be charged, short circuited, or reversed, merely by changing the position of a single handle. The observing telescope has an objective of 28 mm. aperture, and 12.5 cm. focal length, and an eyepiece of 12 mm. focal length. The eyepiece is kept at a fixed distance from the objective (about 25 cm.), and focusing is done by moving the whole telescope forwards or backwards, so that the magnification of the optical system remain the same at all times. The scale in the eyepiece has eighty divisions, and the distance between the extreme divisions of the scale corresponds to an actual distance of 1.022 cm. at the object. The time is measured by a Hipp chronoscope which reads to .002 second, except the very slow times (longer than 120 seconds) which are measured by a stopwatch reading to .2 second.

The substance used for making the spheres is a carefully filtered solution of shellac in alcohol. This solution can be made very thin so that exceedingly small spheres may be made. It is more convenient to use than sulphur, wax, or paraffin, etc., in that heat is not necessary to keep it in the liquid state for atomizing. The alcohol evaporates very quickly, and the density of the spheres reaches a constant value in a very short time. Particles caught on a microscopic slide placed on top of the condenser plates, have been repeatedly examined under a microscope (at about 1,000 diameters) and show perfect sphericity except a few which are distorted by particles of dust or other foreign substances adhering to them, or by being flattened against the microscopic slide before they were completely solidified. Although the radius of the spheres ranges from .0012 to .0030 mm., there is no evidence of lack of homogeneity, as the results of these experiments show. To measure the density of the shellac, a thin coat of it is sprayed on a watch crystal with the atomizer, allowed to dry, and weighed in air and water. Six determinations were made by two observers at different stages of the experiment with varying quantities of the substance, and the results were found to check to within one half of one per cent. of the mean, as is shown by the following table:

Observer.	Quantity in Grams.	Density.
L.....	.3083	1.154
W.....	.1626	1.151
L.....	.3089	1.149
L.....	.0995	1.155
W.....	.1339	1.144
L.....	.4830	1.148
	Mean.....	1.150

This mean value, 1.150, is also within one half of one per cent. of the density of the shellac flakes, from which the solution was made.

THE OBSERVATIONS.

Before and after the taking of an observation on every particle, the potential of the batteries was measured in groups of about 400 cells each by means of a Kelvin and White electrostatic voltmeter having a range of 300 to 900 volts. This voltmeter showed remarkable constancy and all the readings could be duplicated to within 0.5 volt. It was carefully calibrated toward the close of these experiments by comparison with a Weston Laboratory Standard Voltmeter, which was calibrated by the Bureau of Standards just a few days previously, and all voltmeter

readings in these experiments have been corrected by the new calibration curve. The drop of potential of this entire set of storage batteries of 5,000 volts is on the average only 10 volts for an observation of an hour's duration. The potential drop is assumed to be a linear function of the time during an observation so that the potential at any time during the observation may be found by interpolation.

A few seconds after the shellac solution is blown into the chamber with the atomizer, the large particles may be seen in the field of the telescope; but the particles used in these experiments were of such size that it required from 2 to 5 minutes for them to reach the condenser. A careful selection was made to obtain a particle of the proper size and one which showed no flickering, since a particle which flickers is presumably not spherical.

A little shutter (controlled by an electro magnet) above the condenser was closed over the small holes as soon as a particle had been selected, and the electric field was then turned on and off alternately to keep the selected particles in the field of the telescope while all the other particles were allowed to fall to the bottom plate. The speed of the spheres under gravity was then measured by timing it between the two extreme divisions of the scale in the eyepiece of the telescope. It was then brought back to the top and the timing was repeated from 5 to 20 times depending on the speed and the consistency of the observations. The speed of the particle under the force of the elecric field was measured in the same way, except that instead of allowing it to fall under gravity alone after each measurement, the field on the condenser was reversed so that the particles fell under the force of gravity and that of electric field combined. By keeping the electric field on either one way or the other all the time all stray ions, as soon as they are formed, are removed to the plates thus preventing the particle from changing its charge, until a sufficient number of observations of that particular speed have been taken. The charge on the particle was changed by turning on the X-rays, directly behind the window *b*, for a short time. Five or six different speeds in the field are usually taken on each particle, after which its speed under gravity is again taken to check the readings taken at the beginning of the experiments. Tests for convection currents in the space between the condenser plates were made frequently by timing the spheres through the first half and then the second half of the distance and in some cases, particularly in the case of slowly moving particles, timing is done for every one of the eight large divisions in the scale of the eyepiece; but no evidence can be found to support the conjecture that the air in the chamber is not stagnant.

Tables I., II., and III., are typical examples of the observations taken.

TABLE I.

Particle No. 22.

P.D. = 5023.0 volts.
Temp. = 26.8° C.
Pres. = 74.40 cm. Hg.
$1/t_g$ = .043280.
a = .0001774 cm.
l/a = .05507.
$1/pa$ = 75.77.
$e\beta_1$ = 64.41 × 10^{-6}.

t_g	t_f	Mean t_f.	$\frac{1}{t_f}$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_f}\right)$
23.276					
23.090					
23.192					
23.112					
23.110					
23.042					
23.150					
23.122					
23.042					
23.112	24.164				
	24.268				
	24.226	24.188	.041342	10	.008462
	24.122				
	24.162				
	62.588	62.588	.015976	7	.008465
	30.270				
	30.376	30.340	.032960	9	.008471
	30.374				
	40.926	40.899	.024450	8	.008466
	40.872				
	20.108				
	20.080				
	20.030				
	20.088	20.073	.049818	11	.008463
	20.082				
	20.054				
23.114	20.160				
23.042					
23.142					
23.104					
22.940					
22.934					
22.131					
23.050					
23.130					
23.105 = Mean				Mean = .008465	

Column 1 shows the time of fall under gravity (t_g); Column 2 shows the time of rise in the field (t_f) and Column 3 is the mean of the different t_f's. in column 2. Column 4 shows the reciprocals of the number is column 3, and are therefore directly proportional to the velocity in the field.

TABLE II.

Observation No. 26.

P.D. = 5009.5 volts.
Temp. = 23.45° C.
Pres. = 59.27 cm. Hg.
$1/t_g$ = .049541.
a = .0001879 cm.
l/a = .06439.
$1/pa$ = 89.81.
$e\frac{1}{1}$ = 65.14 × 10^{-8}.

t_g	t_f	Mean t_f.	$\frac{1}{t_f}$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_f}\right)$
20.144					
20.142					
20.144					
20.154					
20.188					
20.178					
20.160					
20.244	64.868	64.868	.015416	8	.008120
	42.244	42.222	.023684	9	.008136
	42.200				
	25.006				
	25.010	24.987	.040022	11	.008142
	24.938				
	24.992				
	15.494				
	15.550	15.518	.064441	14	.008142
	15.518				
	15.512				
20.232				Mean.....	.008135
20.086					
20.134					
20.228					
20.228					
20.168					
20.218					
20.228					
20.216					
20.185					

TABLE III.

Observation No. 53.

P.D. = 1660.2 volts.
Temp. = 20.6° C.
Pres. = 12.19 cm. Hg.
$1/t_g$ = .040329.
a = .0001458.
l/a = .3986.
$1/pa$ = 562.48.
$e^{\frac{1}{3}}_1$ = 87.30 × 10^{-6}.

t_g	t_f	Mean t_f.	$\frac{1}{t_f}$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_f}\right)$
24.790					
24.854					
24.862					
24.706					
24.716					
24.712					
24.802					
24.992	39.446	39.538	.025291	14	.004687
	39.630				
	25.478				
	25.226	25.355	.39440	17	.004692
	25.360				
	62.700	62.700	.015949	12	.004690
	48.320	48.379	.020669	13	.004692
	48.438				
	33.368				
	33.596				
24.856	33.260	33.412	.029929	15	.004684
24.756	33.424				
24.714				Mean.....	.004689
24.812					
24.828					
24.840					
24.748					
24.750					
24.796					

THE CALCULATIONS.

It may be seen that equation 3 may be written in the form

$$e_n = K\frac{(v_1+v_2)v_1^{\frac{1}{3}}}{F} \tag{5}$$

or more conveniently

$$e_n = K'\frac{\left(\frac{1}{t_g}+\frac{1}{t_f}\right)\left(\frac{1}{t_g}\right)^{\frac{1}{3}}}{F}. \tag{6}$$

Now if the particle caught say n' additional charges, its time of rise may now be indicated by t_f', so that equation 6 becomes

$$e_{n+n'} = K' \frac{\left(\frac{1}{t_g} + \frac{1}{t_{f'}}\right)\left(\frac{1}{t_g}\right)^{\frac{1}{2}}}{F} \tag{7}$$

and subtracting equation 6 from 7, we have

$$e_{n'} = K' \frac{\left(\frac{1}{t_f'} - \frac{1}{t_f}\right)\left(\frac{1}{t_g}\right)^{\frac{1}{2}}}{F}. \tag{8}$$

Now since $K'/F(1/t_g)^{\frac{1}{2}}$ remains constant throughout the experiment, the successive values of the charge on the particles are proportional to the successive values assumed by the quantity $(1/t_f' - 1/t_f)$ and the value of the elementary charge is obviously equal to the constant $[K'/F(1/t_g)^{\frac{1}{2}}]$ multiplied by the greatest common divisor of all the successive values of $[1/t_f' - 1/t_f]$. When this common divisor is known, the value of n or n' is determined, since n is usually a small number (never more than 30 in these experiments), so that the value of the elementary charge e_1 may now be obtained by dividing equations 6 and 7 by n and $n + n'$ respectively; thus

$$e_1 = \frac{K'}{F} \frac{\left(\frac{1}{t_g}\right)^{\frac{1}{2}}\left(\frac{1}{t_g} + \frac{1}{t_f}\right)}{n}, \tag{9}$$

$$e_1 = \frac{K'}{F} \frac{\left(\frac{1}{t_g}\right)^{\frac{1}{2}}\left(\frac{1}{t_g} + \frac{1}{t_{f'}}\right)}{n + n'}. \tag{10}$$

The mean of the e_1's thus obtained is taken as the true value of the e_1 for the particular particle.

The coefficient of viscosity of air at 23° C. is taken as .0001824. This value was adopted by Millikan for his oil drop experiments, after a very careful study of all the experimental results that are available.

DETERMINATION OF THE CONSTANT A.

It will be observed from equation 3, that e is proportional to the 3/2 power of v, so that if Stokes's law is to be corrected by the term $\{1 + A(l/a)\}$, e_1 must be divided by $\{1 + A(l/a)\}^{\frac{3}{2}}$ in order to give the correct value of e; *i. e.*,

$$e = \frac{e_1}{\{1 + A(l/a)\}^{\frac{3}{2}}} \quad \text{or} \quad A = \frac{e_1^{\frac{2}{3}} - e^{\frac{2}{3}}}{l/a} \div e^{\frac{2}{3}}. \tag{11}$$

If l/a is known for each particle, we can plot the values of $e_1^{\frac{1}{2}}$ as ordinates, and l/a as abscissæ, and if A is a constant, the line joining the values of e_1's would be a straight line, and A would equal to the slope of this line divided by the y-intercept; for obviously, when $l/a = 0$, $e_1^{\frac{1}{2}} = e^{\frac{1}{2}}$. In order to determine this slope as accurately as possible, e_1 should be measured through large ranges of l/a. This is done by decreasing the value of a, that is by using small particles, or by increasing the mean free path by decreasing the pressure of the air in the chamber.

THE VALUE OF THE RADIUS, "a."

To obtain the value of a, the radius of the particle we may substitute for m, its value $4/3[\pi a^3(\sigma - \rho)]$ in equation 2, and solve for a.

$$a = \sqrt[3]{\frac{3Fe}{4\pi g(\sigma - \rho)} \frac{v_1}{v_1 + v_2}}. \qquad (12)$$

It will be seen from this equation, that all the quantities except e are directly measured in each experiment. It will be seen, also, that e enters only in the $1/3$ power in the determination of a, so that a relatively large error in e would not appreciably affect the correct value of a. In these calculations, e is taken as 4.774×10^{-10} e.s.u. (Millikan's value), and the results are shown in column 2 of Tables VII. and VIII.

In the graphs (Figs. 9 and 10), $e_1^{\frac{1}{2}}$ is plotted against $1/pa$ instead of l/a, because of the uncertainty of l, due to the fact that k in the equation $n = knm\bar{c}l$ has not been exactly determined. The correction term to Stokes's law then becomes $(1 + b/pa)$. The value of l/a however is computed for every particle, and is shown in column 8 of Tables IV. and V. For these computations, k is taken as .3502.

SUMMARY OF RESULTS.

Table IV. contains the results of observations on 19 particles, all of which were taken under atmospheric pressure, in the summer of 1913. In this group of experiments, the cover was placed only loosely over the vessel, and no particular care was taken to keep the air dry. Table V. contains the results of 39 observations taken in the following fall, and these last observations were made in a sealed chamber, which was frequently washed with dry air. The pressure varied from atmospheric to 9.65 cm. of mercury, as is shown in column 5 of Table V. The value of $1/pa$ and $e_1^{\frac{1}{2}}$, are shown in columns 6 and 8 of Tables IV. and V., and are plotted in the graphs shown in Figs. 2, 3, and 4. From the slope of this line and its y intercept, $e^{\frac{1}{2}}$ is determined to be 61.03×10^{-8}, and b,

.0007627. The value of A of equation 4, corresponding to this value of b, is 1.067.

TABLE IV.

No.	t_θ	$a\times10^4$ cm.	P. D.	n	P cm. Hg.	$1/pa$	l/a	$e_1^{\frac{1}{3}}$	$e^{\frac{1}{3}}$
1	8.682	2.915	4905.8	25–30	75.13	45.66	.03286	63.03	60.91
2	9.226	2.820	4897.4	22–26	74.54	47.56	.03399	63.07	60.86
3	10.854	2.598	4911.3	18–24	75.05	51.28	.03670	63.39	61.01
4	12.055	2.471	4913.0	16–25	74.98	53.98	.03898	63.36	60.75
5	13.743	2.303	4912.9	13–16	75.05	57.87	.04136	63.55	60.87
6	14.830	2.216	4916.4	12–18	75.09	60.10	.04313	63.76	60.99
7	14.955	2.205	4912.7	12–16	75.00	60.45	.04354	63.97	61.16
8	16.126	2.126	4912.5	9–15	75.39	62.40	.04500	63.93	61.04
9	16.688	2.081	4951.0	10–15	75.05	64.04	.04570	64.05	61.08
10	17.916	2.030	4904.6	9–15	74.89	66.31	.04760	63.93	60.85
11	19.753	1.910	4900.0	8–13	74.58	70.21	.05011	64.22	60.97
12	22.308	1.795	4916.2	6–13	75.20	74.20	.05351	64.48	61.04
13	25.061	1.689	4888.0	6–9	75.18	78.79	.05664	64.69	61.03
14	28.208	1.594	4087.3	5–12	74.91	83.78	.06007	64.75	60.70
15	30.650	1.527	4913.2	4–9	75.13	87.15	.06253	64.87	60.83
16	31.935	1.500	4910.7	4–7	74.98	88.94	.06432	64.99	60.87
17	36.936	1.384	4085.3	4–9	74.91	96.43	.06927	65.64	61.17
18	40.300	1.325	4919.2	3–6	75.39	100.14	.07220	65.64	61.00
19	46.278	1.235	4902.6	4–6	74.89	108.08	.07758	65.74	60.72
							Mean.....		60.939

The question may be raised as to whether the alcohol evaporated from the shellac solution may not effect the pressure of the air in the chamber, and hence the slope of the line in Figs. 2, 3, and 4. That the alcohol vapor has no appreciable effect on the observations with the shellac

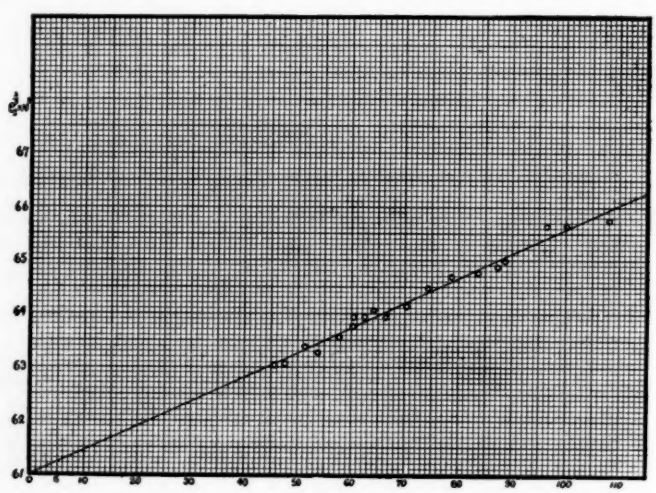

Fig. 2.

TABLE V.

No.	t_g	$a \times 10^4$ cm.	P. D.	n	P	$1/pa$	l/a	e_1^3	e^3
20	13.300	2.347	5006.7	14–19	74.40	57.28	.04162	63.64	60.98
21	17.271	2.051	5014.0	10–17	75.66	64.43	.04616	63.91	60.92
22	23.105	1.774	5023.0	7–11	74.40	75.77	.05507	64.41	60.90
23	27.453	1.612	5013.7	5–11	75.66	81.99	.05892	64.82	61.02
24	19.556	1.909	5006.6	7–13	59.86	87.52	.06236	65.14	61.08
25	30.682	1.527	5014.4	5–8	74.40	88.00	.06396	65.17	61.09
26	20.185	1.879	5009.5	8–14	59.27	89.81	.06439	65.14	60.97
27	34.810	1.427	5013.4	4–7	75.66	92.62	.06653	65.54	61.24
28	25.850	1.787	5014.7	6–9	54.25	103.06	.07388	65.65	60.87
29	43.932	1.267	5005.0	3–7	74.50	105.93	.07596	65.70	60.78
30	22.279	1.779	4186.0	9–14	48.89	114.97	.08273	66.16	60.82
31	55.020	1.122	5004.7	2–6	75.28	118.41	.08484	66.98	61.49
32	21.600	1.792	4176.0	9–14	43.73	127.63	.09142	67.08	61.16
33	22.096	1.769	4176.0	8–12	40.76	138.69	.1000	67.38	60.94
34	20.960	1.805	4178.8	9–12	39.35	140.76	.1007	67.84	61.31
35	19.164	1.895	4181.8	9–13	35.45	148.87	.1071	67.51	60.60
36	20.787	1.821	4192.0	8–12	34.97	157.06	.1130	67.90	60.61
37	22.655	1.727	4180.8	7–11	33.93	170.63	.1220	68.53	60.61
38	25.829	1.604	3317.5	7–13	36.17	172.33	.1216	69.06	61.06
39	19.380	1.810	3348.4	11–16	29.00	180.57	.1294	69.76	61.38
40	20.140	1.852	3343.8	12–16	28.15	196.25	.1406	70.27	61.16
41	20.428	1.791	3352.4	10–14	26.56	210.19	.1505	70.74	60.98
42	21.850	1.715	3334.4	9–13	25.18	231.64	.1660	72.22	61.47
43	11.758	2.326	3243.5	21–25	18.08	237.74	.1685	72.35	61.31
44	19.500	1.814	3347.2	11–17	22.82	241.58	.1732	72.33	61.11
45	23.366	1.629	3260.0	8–12	21.33	287.88	.2035	74.18	60.82
46	17.656	1.847	2488.2	15–19	16.50	328.14	.2333	76.62	61.39
47	23.134	1.592	2500.0	9–14	16.46	381.52	.2719	78.79	61.08
48	29.924	1.394	2486.1	7–13	18.23	394.49	.2810	79.38	61.07
49	25.080	1.523	3220.0	7–18	16.40	400.33	.2834	79.07	60.48
50	20.220	1.671	2523.7	12–18	14.50	412.68	.2951	81.14	62.04
51	28.800	1.405	3150.0	6–15	16.43	433.10	.3064	80.87	60.86
52	19.557	1.607	2494.5	10–15	12.34	481.57	.3414	83.17	60.81
53	24.796	1.458	1660.2	12–17	12.19	562.48	.3986	87.30	61.19
54	27.398	1.390	2482.3	6–13	12.78	562.98	.4015	87.36	61.22
55	28.360	1.449	2509.0	6–10	10.74	644.67	.4619	91.05	61.12
56	21.602	1.535	1663.6	14–22	10.04	649.00	.4596	90.45	60.32
57	19.855	1.593	1661.4	14–26	9.65	650.60	.4607	91.36	61.16
58	25.550	1.406	2483.3	7–11	10.75	661.63	.4733	91.74	61.02
								Mean e^3 =	61.024

spheres is shown by the fact that *drying materials* placed in the chamber produced no different result in the observations, and that experiments with beeswax[1] and other substances containing no volatile vapors gave a line of the same slope as shown in Figs. 2, 3, and 4.

[1] Beeswax was used for making these experiments several months before shellac was adopted, and fair consistency of results is obtained. The main difficulty is the uncertainty of the density of the small particles employed. One would naturally think that particles of

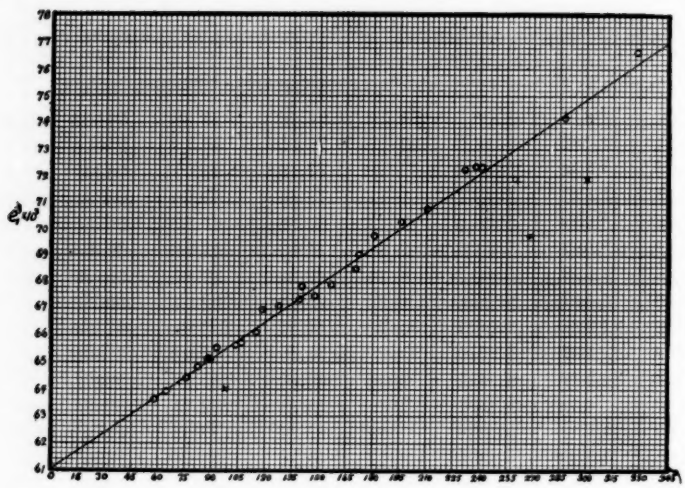

Fig. 3.

Tables IV. and V. include all the observations that were taken and calculated in the period of about seven months, except two observations (shown as crosses in the graph), which were so far from the line joining the rest of the observations that there is every reason to believe that they were dust particles or other foreign substances. There was also a

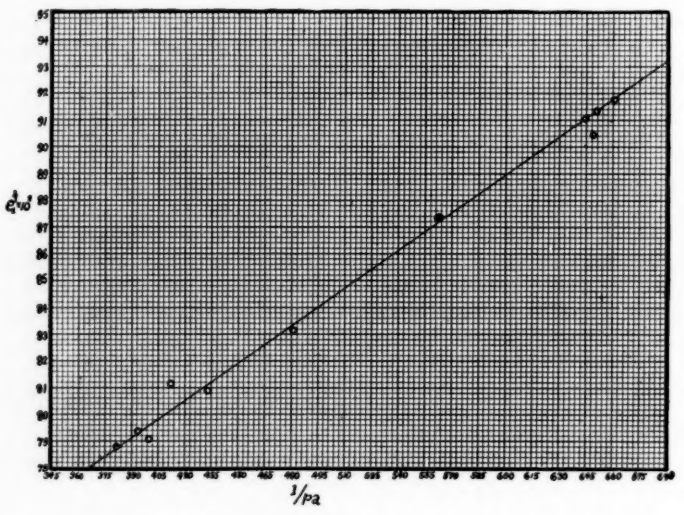

Fig. 4.

the order of .002 mm. in diameter would have the same density as the cold solid mass, a short time after they were blown from the atomizer. As a matter of fact, their density does not reach a constant value for an hour or more after they were blown, as may be shown by suspending one of them between the condenser plates with the electric field, and measuring its rate of fall under gravity, every now and then.

group of observations which appeared very erratic, and which upon investigation was found to be due to some oil, from the constant temperature bath, leaking into the chamber through the valve between the atomizer and the vessel, so that some of the observations were on oil drops instead of on shellac spheres. For the sake of certainty, however, all the observations taken from the first appearance of the lower values, to the overhauling of the apparatus, 16 in number, were discarded.

A more accurate method to determine the value of $e^{\frac{3}{2}}$ than the graphical evaluation, is to reduce each of the observations on $e_1^{\frac{3}{2}}$ to $e^{\frac{3}{2}}$, by means of the above value of b and the equation

$$e^{\frac{3}{2}}\{1 + (b/pa)\} = e_1^{\frac{3}{2}}. \qquad (13)$$

The results of this reduction are shown in column 9 of Tables IV. and V. The mean of the values of $e^{\frac{3}{2}}$ obtained from observations 1 to 19 inclusive, is 60.939×10^{-8} making $e = 4.758 \times 10^{-10}$, while observations 20 to 58 give $e^{\frac{3}{2}} = 61.024 \times 10^{-8}$, and $e = 4.767 \times 10^{-10}$. The mean of all observations is

$$e = 4.764 \times 10^{-10} \text{ e.s.u.}$$

This value agrees to within one-fifth of one per cent. with the value obtained by Millikan with the oil drops and the uncertainty in the density of the shellac is one half of one per cent. so that the difference is well within the limits of experimental error. The value of A, however, is about 20 per cent. higher than Millikan's value, and this can be explained only by assuming that the coefficient of slip between oil and air is different from that between shellac particles and air.

M. Jules Roux[1] has obtained a value of 1.64 for this constant A by measuring the rate of fall of sulphur spheres first in air and then in a liquid (xylol). He assumed that Stokes's law holds for the motion of the spheres in the liquid, and thus calculated the radius a. Then with this value of the radius, he calculated the speed which the particle should have in air if Stokes's law held, and by comparing this speed with the actual observed speed, he found the correction term $\{1 + A(l/a)\}$. The error in the determination of A is thus the error in the difference between these two speeds. Now the time intervals in Roux's measurements were from 3 to 5 seconds—and the differences between the calculated and the observed speeds were about 0.4 second. Further he made but one single time measurement upon each drop; he records observations upon but 5 drops in all, and his measurements were all made with a stopwatch, which read to .2 second, so that his possible error would be .2 second for starting

[1] J. Roux, Annal. de Chim. et de Phys., 8th series, Vol. XXVIII., 69–132, May, 1913.

and .2 second for stopping, making .4 second in all, *or just enough to cover the entire value of the constant which he was trying to determine.* Since then his possible error was 100 per cent. it is evident that his results are in entire agreement, *within the limits of observational error*, with the present work which locates the value of A with an uncertainty of say 2 or 3 per cent. As to Roux's determination of e with sulphur spheres by Millikan's method it need only be said that it is based on the value of A just described. Further his mean value (4.17×10^{-10}) is obtained from observations on only eight particles, and the results, aside from involving the incorrect value of A, are not consistent enough to justify the belief that they are comparable in accuracy with the results of the oil drop experiments.

I wish to express my sincere thanks to Professor Millikan for his kind assistance and counsel throughout these experiments, and I also take pleasure in acknowledging the able assistance of Mr. C. W. White, and Mr. H. L. Wilson in making some of the above observations.

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DIURNAL AND ANNUAL VARIATIONS IN OVERLAND RADIO-TRANSMISSION.

By A. H. Taylor.

IT is a fact well known among radio operators that the winter range of a wireless station greatly exceeds its mid-summer range.

This is partly due to the prevalence of "strays" during the summer season, especially on the long wave-lengths, and partly due to a real difference in transmission, which may perhaps be ascribed to a difference in absorption brought about by different conditions of earth and atmosphere during summer and winter.

Most quantitative experiments so far in long distance work have, for obvious reasons, been with oversea transmission, since a ship station at definite adjustment may be sent out to great distance from a land station sending at constant power, thus making possible, as in the experiments of Austin,[1] a series of measurements under similar conditions at the receiving station, varying only the distance between the two. This method of procedure is obviously impossible for long distance overland transmission, although it is possible in shorter distance field tests. Austin represents the oversea transmission as being quite constant in the daytime, and following the law

$$i_2 = \frac{K i_1 \epsilon^{-\frac{KD}{\sqrt{\lambda}}}}{\lambda D},$$

when i_2 is the received current, to the square of which the audibility may be taken as proportional. The constant K depends on the heights to center of capacity of sending and receiving antenna, the type of antenna used, and the equivalent resistance of the receiver, while i is the sending current and λ the wave length in kilometers. D is the distance between stations, also in K.M. Application of this formula to the 3,500 m. wave so frequently used this spring by Arlington (NAA) in correspondence with Key West (NAR) indicates that it should suffer a thirty-six fold loss in audibility due to absorption in traversing an oversea distance equal to the overland distance between Grand Forks and Washington. Some roughly quantitative results calculated from observations taken here on this wave indicated that it was received nearly 120 times stronger

[1] Bull. Bur. Standards, Vol. 7, No. 3.

at midnight than at noon. This estimate is based on shunted telephone readings, using a single 800 foot aerial wire of seven strands of No. 22 phosphor bronze, far end 120 feet in height, near end 65 feet. An audion detector was used and a 3,200Ω New Navy type telephone receiver. The signals were barely distinctly audible at noon, but the best midnight (or thereabouts) readings showed shunts of as low as 14Ω. Bearing in mind Braun's[1] recent criticism of shunted telephone readings, the writer can hardly give these results weight enough to attempt to calculate the absorption coefficient for this wave, especially since it is far from safe to assume the midnight transmission to be unabsorbed. They do indicate, however, that the average daylight transmission was fully four to five times as much absorbed as it should have been in an equal oversea distance, according to the Austin formula. Furthermore, as anticipated in a previous paper,[2] the daylight transmission overland is most certainly affected by the weather and the time of year, and is by no means as constant as oversea transmission.

In this connection it is of interest to note that the noon time signal from N A A at 2,500 m., $i. = 87A$, $p = 52$ K.W. could not be received here on the single-wire aerial without the use of a second audion used to amplify the first, while the 3,500 m., $i = 104A$, $P = 58$ K.W., an hour later was distinctly audible, with one audion. This shows that the shorter wave suffers even greater absorption.

I am greatly indebted to Captain Bullard, U. S. N., for data on the 3,500 m. wave.

At the present time, June 20, in order to get the 11:00 A.M. (Central time) or noon time signal at 2,500 m., we are obliged to use a 3-wire 800 foot aerial, although in midwinter a small 150 foot aerial sufficed.

I have no hesitation, therefore, in asserting that the daylight transmission between here and Washington is many times stronger in winter than in summer, this statement being based on comparative shunted telephone readings on the two aerials, long and short, indicating that for Sayville, N. Y., 2,800 meters, the long aerial is seven times as effective as the short one. The long aerial having been recently installed, to cope with summer conditions, no winter observations have yet been taken on it. This long aerial points S. E. and is, therefore, unfavorably directive, else it would be even more efficient.

From observations on Arlington, Va., 1,400 miles, and Key West, Fla., 1,840 miles, it would seem that annual variations are dependent on the character of the country traversed. In midwinter the 2,500 m. wave $i = 57A$, $P = 52$ K.W. of Arlington, received on the smaller aerial,

[1] F. Braun, Yahrbuch d. drahtlosen Teleg. und Telephonie, April, 1914.

[2] Taylor, PHYS. REV., May, 1914.

equivalent resistance 40Ω, was very little stronger, and indeed frequently not as strong as the 1,800 m. $i = 37\ A$, $P = 23$ K.W. wave of Key West. (The equivalent aerial resistance for 1,800 m. wave 27Ω) I am indebted to Captain J. L. Jayne, U. S. N., for the data on these waves. I am not informed as to the height to the center of capacity at Key West, but for the purpose of argument, assuming it to be the same, the relative intensities of these two waves should be as

$$\frac{i^2}{\lambda^2 D^2 \cdot R} = 2.7 \times 10^{-6}$$

for N A A (Arlington), and $n = 1.8 \times 10^{-6}$ for N A R, Key West, neglecting absorption. With absorption at 1,800 meters in all probability greater than at 2,500 m. N A A should have been heard much louder than N A R. These observations were taken between 9:00 and 9:45 P. M., Central time. As the spring came on, a marked change in this relation came about. Both stations averaged weaker and weaker, finally frequently necesstating the use of the double audion detector or amplifier, but N A R faded much faster than N A A, becoming at that hour seldom audible after April 1, so that from approximate equality in intensity, the signals of Key West were in the course of three months reduced to less than one tenth the intensity of those of Arlington. The writer can scarcely believe that this difference can be attributed entirely to difference in wave-lengths, unless at the same time we assume that the absorption in the Mississippi Valley, which offers a remarkably preferential highway for radio-transmission in winter, increased much more rapidly than that over the more northerly path between here and Washington.

It has occurred to the writer that the loosening up of the ground by plant growth in the spring, and even the growth itself, may be accompanied by a certain amount of ionization from radioactive sources, thus accounting for the almost sudden increase of absorption of electromagnetic waves which occurs in the spring. This effect would be more noticeable over a southerly route.

The preferential winter transmission in the direction of the Gulf of Mexico to Grand Forks, may be due to high soil conductivity in the lower half of the Mississippi Valley, brought on by abundant rainfall. The generally level nature of the country is also unquestionably an aid.

Several investigators mention in recent papers the fact that river valleys, such as the Rhine and Rhone, offer preferential paths. Among these might be mentioned M. Reich,[1] who mentions a distinct difference in transmission between Göttingen and Köln, and Göttingen and Strass-

[1] M. Reich, Phys. Zeitschrift, 14, 1913.

burg, while he attributes to the fact that a valley favors, for a great part of the distance, the transmission from Strassburg to Göttingen. The writer does not, therefore, advance the idea of the preferential Mississippi Valley path as anything new, but wishes rather to call attention to the fact that, judging from the Key West signals, this preference, so striking in the winter, disappears quite completely in the spring.

Since it usually happens that the transmission rises rapidly after sunset, it might be urged that the whole matter might be accounted for by the difference in time of sunset between Washington and Key West.

This difference is, however, only about one fourth the total difference between Washington and Grand Forks, and seems insufficient to cause any great difference. In order to be sure of this point, the Key West signals were usually followed, when possible, to nearly 10:30, Central time, with marked increase in intensity, although not nearly enough increase even then to compare favorably in the spring with the 9:00 Arlington signals.

It must be noted, in reference to the inconstancy of daylight transmission, that Austin distinctly states that for oversea transmission the daylight transmission is exceedingly constant.

His experiments over long distances would seem to prove this quite conclusively, but his experiments have not, to the knowledge of the writer, been repeated across equally long distances entirely overland. The investigations of H. Mosler,[1] on the annual and daily variations in the intensity of signals from Nordeich and the Eiffel tower led him to conclude that the intensity in the daytime was essentially constant, and varied little if any during the year. This absolutely erroneous conclusion is due to the short distance of only a few hundred kilometers, over which his signals were received. If the absorption is, as seems to be generally accepted, a logarithmic function of the distance, which holds also for Sommerfeld's surface wave, then variations scarcely perceptible at 300 K.M. will be very great at 3,000 K.M. As for the daily variation at Grand Forks of the Arlington 11:00 A.M. Central signal, while it is by no means as great as the variation from summer to winter, yet variations of threefold in the intensity are now being observed, and an attempt is being made to correlate these diurnal variations with weather conditions.

During the month of April Arlington was not only heard frequently on 3,500 m. at 1:00 P.M. but also at 6:00 P.M., and almost invariably with greater intensity, in the ratio of two or three to one. This may be due to the fact that twilight had already begun at Arlington.

[1] H. Mosler, Electrot. Ztschr., 35, 1913.

Summary.

1. Overland daylight absorption of electromagnetic waves is several times greater than oversea absorption calculated from the Austin formula.

2. Overland daylight absorption is, unlike oversea absorption, not constant.

3. Overland daylight transmission on long waves is much stronger between Grand Forks and Washington (1,400 miles) in winter than in summer.

4. Overland nocturnal transmission varies with the time of year to a different degree, depending on the nature of the country traversed.

5. The Mississippi Valley shows a very wide variation in summer and winter transmission.

RADIO STATION 9YN,
UNIVERSITY, N. D.
July 15, 1914.

A DETERMINATION OF AVOGADRO'S CONSTANT N FROM MEASUREMENTS OF THE BROWNIAN MOVEMENTS OF SMALL OIL DROPS SUSPENDED IN AIR.

BY HARVEY FLETCHER.

INTRODUCTION.

In a previous paper[1] equations were developed which showed the effect of the so-called Brownian movements upon a spherical particle moving under the influence of a constant outside force. In these formulæ there occurred a factor k which was a function of l/a, the exact dependence being unknown at the time the paper was written. For this reason the experimental work was directed toward determining Ne, which process did not involve k. Since that time Prof. Millikan, by a series of careful experiments, has determined the form of the function[2] k; and has thus made possible a fairly exact determination of N by the Brownian movement method as applied to gases.

The former equations have been modified so that the task of finding the Brownian movement effect is now much less laborious than before. Also the apparatus has been improved, making it possible to obtain from 1,000 to 6,000 observations on a single particle.

§ 1. DEDUCTION OF THE EQUATION FOR THE DETERMINATION OF N.

It was shown in the article cited above that the law of distribution of the times of fall through a constant distance of a small spherical particle which is subjected to the bombardment of gas molecules is

$$n = \frac{\mathcal{N}}{2}\sqrt{\frac{h}{\pi}}\int_{t_2}^{t_1}(bt^{-\frac{3}{2}} + Vt^{-\frac{1}{2}})e^{-h/t(b-Vt)^2}dt, \tag{1}$$

where

$$h = \frac{9\pi\mu ak}{4\epsilon} = \frac{3}{2}\frac{\pi\mu akN}{RT}. \tag{2}$$

In this formula n is the number of times, out of $\mathcal{N}$ observations, that the particle will fall a constant distance b in a time which lies between t_1 and t_2; V is the constant velocity due to gravity and may be found

[1] PHYS. REV., Aug., 1911, p. 81.

[2] PHYS. REV., Vol. II., p. 109, 1913, gives the method and PHYS. REV., Vol. I., p. 219, 1913, gives the results on k. See also Le Radium, *10*, p. 15, 1913.

experimentally as shown later; h is a constant depending upon the number of molecules N in a gram molecule of the gas, the viscosity coefficient μ, the gas constant R, the absolute temperature T, and the function k as indicated in equation 2. The method of finding a and k will be outlined in another section.

Let the time of fall due to gravity,

$$\frac{b}{V} = t_g. \tag{3}$$

Now the average value of all the observed times of fall below t_g will be given by

$$t_a = \frac{1}{2}\sqrt{\frac{h}{\pi}}\int_{t_g}^{0} t(bt^{-\frac{3}{2}} + Vt^{-\frac{1}{2}})e^{-h/t(b-Vt)^2}dt.$$

Change the variable from t to u by the relation $b = Vt + ut$ and we get

$$\bar{t}_a = 2\sqrt{\frac{h}{\pi}}\int_0^{\infty} \frac{2u^2 + 4bV - 2u\sqrt{u^2 + 4bV}}{4V^2} e^{-hu^2}du. \tag{4}$$

Similarly, the average value of all the observed times of fall above t_g is given by

$$\overset{+}{t}_a = 2\sqrt{\frac{h}{\pi}}\int_{-\infty}^{0} \frac{2u^2 + 4bV - 2u\sqrt{u^2 + 4bV}}{4V^2} e^{-hu^2}du. \tag{5}$$

Evaluating (4) and (5) we have

$$\overset{+}{t}_a = \frac{b}{V} + \frac{1}{4hV} + \frac{1}{V^2}\sqrt{\frac{h}{\pi}}\int_0^{\infty} u\sqrt{u^2 + 4bV}e^{-hu^2}du,$$

$$\bar{t}_a = \frac{b}{V} + \frac{1}{4bV} - \frac{1}{V^2}\sqrt{\frac{h}{\pi}}\int_0^{\infty} u\sqrt{u^2 + 4bV}e^{-hu^2}du.$$

Adding we have

$$\frac{\overset{+}{t}_a + \bar{t}_a}{2} = \frac{b}{V} + \frac{1}{4hV^2}. \tag{6}$$

Theoretically this equation in connection with equation (2) could be used to determine N, but the difference between $\left(\frac{\overset{+}{t}_a + \bar{t}}{2}\right)$ and b/v is so small that it is not well adapted for this purpose.

Let $\tau = \left(\frac{\overset{+}{t}_a - \bar{t}_a}{2}\right)$, then

$$\tau = \frac{1}{v^2}\sqrt{\frac{h}{\pi}}\int_0^{\infty} u\sqrt{u^2 + 4bv}e^{-hu^2}du. \tag{7}$$

If the variable is changed by the relation $hu^2 = x$, and the substitution

$$z^2 = 4hbv \tag{8}$$

is made, there results

$$\tau = \frac{2}{\sqrt{\pi}} \frac{t_0}{z^2} \int_0^\infty \sqrt{x + z^2} e^{-x} dx.$$

If we expand the integrand and integrate the resulting series we obtain

$$\tau = \frac{t_0}{z^2} \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x} \left(1 + \frac{1}{2}\frac{x}{z^2} - \frac{1}{8}\left(\frac{x}{z^2}\right)^2 + \frac{1}{16}\left(\frac{x}{z^2}\right)^3 \cdots\right) dx$$

$$= \frac{t_0}{z} \frac{2}{\sqrt{\pi}} \left(1 + \frac{1}{2z^2} - \frac{1}{4z^4} + \frac{3}{8z^6} + -\right)$$

or

$$z = \frac{t_0}{\tau} \frac{2}{\sqrt{\pi}} \left(1 + \frac{1}{2z^2} - \frac{1}{4z^4} + \frac{3}{8z^6}\right). \tag{9}$$

This expresses z in terms of itself; but inasmuch as the term $1/2z^2$ is usually of the order .02, the formula

$$z = \frac{2}{\sqrt{\pi}} \frac{t_0}{\tau}$$

may be used to get an approximate value of z, and if then this value is substituted in the brackets a more accurate value may be obtained which may again be substituted in the brackets. We thus arrive at a value of z in terms of t_0 and τ which can be determined from experiment. Comparing (9) with (8) and (2) we see that

$$N = \frac{RT}{6\pi\mu} \frac{z^2}{akV^2 t_0}. \tag{10}$$

For air this reduces to

$$N = 7.12 \times 10^{12}\{1 + .0008(t - 20)\} \frac{p^2}{akV^2 t_0}.$$

Comparing (2), (6) and (9), we get

$$\frac{\overset{+}{t}_a + \overset{-}{t}_a}{2} = t_0 + \frac{1}{3}\frac{t_0}{z^2}. \tag{11}$$

This equation is of theoretical interest only and can be checked by experiment. In the observations recorded below, it is nearly always found that $(\overset{+}{t}_a + \overset{-}{t}_a)/2$ is greater than t_0 by a quantity of the order of magnitude indicated in this equation.

All of the quantities of the right-hand member of equation (10) can be measured by experimental methods to be described later.

§ 2. METHOD OF CALCULATING a AND k.

Prof. Millikan gives[1] for the value of k,

$$k = \left\{ 1 + \frac{l}{a}(.874 + .32e^{-1.54a/l}) \right\}^{-1} \tag{12}$$

and deduces l from the Boltzman equation $\mu = .3506\rho\bar{c}l$. If we combine this with the pressure equation $p = \frac{1}{3}\rho c^2$ and remember that $\bar{c} = .921c$ we get for air the equation

$$l = \frac{\mu}{.919p\sqrt{\frac{3\rho_0}{p_0}}} = \frac{70.5}{p} \times 10^{-5}\{1 + .00446(t - 20)\}, \tag{13}$$

where p is expressed in centimeters of mercury and t is the number of centigrade degrees above 20° C.

When gravity is the only force acting, we have from Stokes's law of fall

$$mg = 6\pi\mu akV.$$

Write equation (12) in the form

$$k = \left(1 + \frac{B}{a}\right)^{-1} \tag{14}$$

where

$$B = l(.874 + .32e^{-1.54a/l}),$$

and substitute in the above and solve for a. Then

$$a = -\frac{B}{2} + \sqrt{\left(\frac{B}{2}\right)^2 + \frac{9}{2}\frac{\mu V}{\rho g}} = -\frac{B}{2} + \sqrt{\frac{B}{2} + .921 \times 10^6 V}. \tag{15}$$

To determine a from (14) and (15) first neglect the exponential term to get an approximate value of B; substitute this in (15) to obtain an approximate value of a; then substitute this in (14) thus giving a more accurate value of B, and repeat the process until the desired accuracy is obtained. In most cases this need only be repeated once and at most twice. a and B are then substituted in 13 to obtain k.

§ 3. DESCRIPTION OF APPARATUS.

The apparatus is similar to Professor Millikan's and to that used in my previous experiments on the Determination of Ne for Gaseous Ioniza-

[1] PHYS. REV., 1, p. 218, 1913. Also Le Radium, *10*, p. 15, 1913.

tion with some important modifications. It consists essentially of four parts, the lighting system, the observing system, the timing system, and the vessel containing the small oil drops suspended in air. The lighting system is the same as used before. The light from a 15-ampere direct current arc is passed through a condensing lens, then through a column of water to absorb the heat, and then between the condenser plates to illuminate the drop (See Fig. *B*, p. 93, PHYS. REV., Aug., 1911). The arc is held in position by means of two tangent screws at right angles, which enables one to adjust it to any desired position.

The observing telescope, which was made by Wm. Gaertner and Company especially for this experiment, is mounted on a cathetometer. In addition to the two tangent screws ordinarily found on this instrument, namely one for changing the heighth and the other for changing the azimuth, the telescope is mounted on a ratchet and pinion which enables one to move it back and forward without changing the magnifying power, *i. e.*, without changing the distance between the objective and eye piece. The objective is corrected for the distance for which it is used, namely about ten inches. In the eye piece is mounted a scale having ten large divisions each divided into five equal parts. After each set of observations this scale is calibrated by comparison with a standard centimeter.

The time is taken by means of a kymograph. The paper which is to receive the record is mounted on two slowly revolving drums which are placed about three feet apart, and it is then covered with lamp black. By means of a signal key the time when the small oil droplet crosses each division in the eye-piece is recorded on the kymograph. Fig. 1

Fig. 1.

shows a photograph of a very small part of the record after it has been fixed with shellac.

The complete record measures 90×8 inches. The time marker was compared with a standard clock and found to agree to one fortieth per cent.

Fig. 2 shows a vertical cross section of the vessel in which the small

[1] PHYS. REV., Aug., 1911.

oil drops are suspended. The chamber B is exhausted to the desired pressure and the stopcock C_2 is closed. A fine spray of liquid vaseline is produced in the bottle A by means of an ordinary atomizer. The cock is then opened, permitting part of the spray to pass along the tube into the chamber B, and to finally fall through the small hole in the top plate of the condenser into the position indicated in the figure. Here the

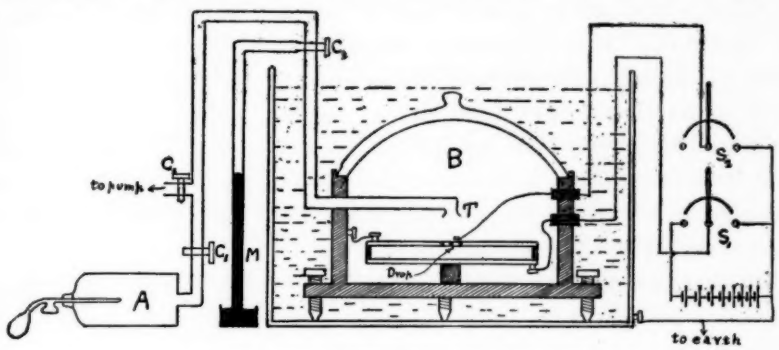

Fig. 2.

spray is illuminated and observed as described above. During the observation the three-way stopcock C_3 is turned so that the vessel and pressure gauge M are in communication. The entire vessel containing the condenser plates is closed at the top with a bell jar and immersed in a bath of transformer oil. This serves two purposes; it stops small leaks which might exist at the different joints, and keeps the air in the vessel at a constant temperature—thus preventing convection currents.

In order to control the drop with electric forces, it is necessary that it be charged. To prevent it from remaining uncharged in case it should catch an ion from the air an X-ray bulb is arranged so as to produce intense ionization between the plates making it possible for the drop to become quickly recharged. However it was found that for pressures under 20 cm. of mercury that the drop very seldom caught ions from the air. In fact only two of the drops recorded in this paper changed their charge, although some of them were under observation six hours.

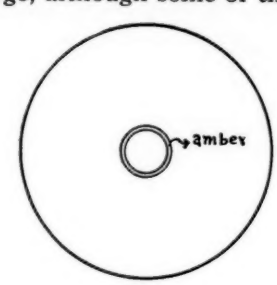

Fig. 3.

Fig. 4.

To enable one to raise the drop after it had fallen, a condenser of dimensions like that used by Professor Millikan in all the oil drop work was employed. It was found that the small droplets, due to Brownian movements, would sometimes drift to the right or left and finally go out of the beam of light and be lost. To prevent this the top plate was cut into two concentric circular plates which were insulated from each other by a thin strip of amber as indicated in Fig. 3. If a negatively charged drop should drift in any direction whatever from the center of the condenser, the switch S_1, is thrown to the right, and the switch S_2 to the left, producing an electrostatic field similar to that shown in Fig. 4. The drop would be forced back again into the center of the beam of light. The switches would just be reversed for a positively charged drop. This precaution was justified for the drop was shifted from three to ten times during the progress of a set of observations.

With these precautions it was found that a drop could be held under observation for almost an unlimited time. One drop was under observation six hours and if we had so desired we could have held it twice that long as the seeing was just as good at the end as it was at the beginning.

§ 4. THE DATA.

The density of the liquid vaseline was found to be .845 gm./cm.^{3} at 20° C.; the viscosity coefficient of air was taken as .0001826 at 23° C.; and the gas constant R, as 82.9×10^6. Because of the large amount of space that would be taken the complete data is not given but only the final values. Table I. shows a sample of the original data as it was read from the kymograph record. It is the first 100 observation on drop 1. In the first column is recorded the time at which the drop crossed each scale division. It was found impracticable to permit the drop to fall the full fifty divisions, as it would drift slightly out of focus and in the process of refocusing the scale would be shifted. So that the breaks in the column represents periods of refocusing or some other difficulty, while from one break to the next represents a continuous falling of the drop under the influence of gravity. For example, the first time it fell 24 divisions in 71.0 seconds, and was then brought back by the electric field. It then fell 23 divisions in 72.1 seconds; 45 divisions in 131.3 seconds; and 25 divisions in 75.6 seconds; etc. The time of fall t_g for one division due to gravity was obtained by dividing the total distance of fall by the number of divisions crossed, *i. e.*, in this case

$$t_g = \frac{71.0 + 72.1 + 131.3 + 75.6 + \text{etc.}}{24 + 23 + 45 + 25 + \text{etc.}} = 3.092.$$

In the second, third, and fourth columns are recorded the times necessary to travel each scale division, each two scale divisions, and each three scale divisions respectively. These times are derived from the first column in a very obvious manner. The average of all of the values in the first column above 3.09 is found to be 3.587, while the average of those below 3.09 is 2.661. These values are designated $\dot{t}_a$ and $\bar{t}_a$ and are tabulated in Table II. Then

$$\tau = \frac{3.587 - 2.661}{2} = .463 \text{ second.}$$

z can now be computed from equation 9 and is found to be 7.58. If this value is substituted in (10) there results for N, 60.9×10^{22}. The velocity V is simply the fall distance .00916 divided by 3.09 or .002962 cm./sec. From this value a and k can be computed as explained in Section 2. The final values for this drop are tabulated in Table II. It is interesting to note that z for the three different fall distances is proportional to 1, 1.408, and 1.697 *i. e.*, to 1, $\sqrt{2}$, and $\sqrt{3}$ as it should be according to equation (10).

The amount of labor that was necessary to obtain a value of N according to the original method of calculation can be partly realized when it is pointed out that Table I. contains only one seventh of the observations on this drop (Drop 12 has five times as many observations) and that each observation required a separate calculation[1] to obtain a value of u, and finally an average of all of these values of u had to be found. It still requires considerable time to work up the data, but by using the adding machine one can add 1,000 numbers in a comparatively few minutes.

Tables II. to XIII. contain the final values obtained from observations taken during the last three months. This represents all of the data taken during this time with the exception of two drops, the first being discarded because it was lost when only a few observations were taken; the second being discarded because the seeing was poor and consequently inaccurate timing resulted. At the top of each table are given the constants a and k obtained from the velocity V. In the different columns are given the average values obtained from Brownian movements.

Particular attention is called to Drop 12, the last drop which was observed. As is seen from the table we obtained 5,950 observations on the time of fall through ten different fixed distances. In order to bring out more clearly the fact that z is proportional to $\sqrt{t_g}$ the value of $z/\sqrt{t_g}$ is recorded in the 7th column. Although there is some little

[1] $u = \frac{V(t_g - t)}{\sqrt{t}}$ equation 28 of the art. already cited.

TABLE I.

Time.	1 Division.	2 Division.	3 Division.	Time.	1 Division.	2 Division.	3 Division.
				36.10	2.30		8.90
0.20				38.40	2.80	4.90	
3.20	3.00	5.40	7.70	41.20	2.10		
5.60	2.40			43.30	3.90	6.80	
7.90	2.30	5.70	9.7	47.20	2.90	5.60	9.70
11.20	3.40			50.10	2.10		
14.80	3.50	6.30		52.20	3.20		
17.60	2.80		8.40	55.70	3.30	6.20	
20.70	3.10	5.60		59.00	2.90		10.00
23.20	2.50			61.90	3.00		
26.00	2.80	5.50	9.60	64.90	2.90	7.00	
28.70	2.70			67.80	4.10	6.70	9.20
32.30	3.60	6.90		71.90	3.60	6.70	
35.60	3.30		9.70	75.50	3.10		
38.70	3.60	7.40		78.60	2.50	5.30	9.10
43.00	4.30			81.10	2.80		
45.30	2.30	4.80	7.50	83.90	3.00	6.30	
47.80	2.50			86.90	3.30		6.70
49.90	2.10	5.00		90.20	2.70	4.70	
52.80	2.90		8.20	92.90	2.00		
56.10	3.30	5.90		94.90	2.00	4.30	8.60
58.40	2.30			96.90	2.30		
61.00	2.60	6.40	10.20	99.20	3.80	6.30	
64.80	3.80			103.00	2.50		9.00
67.70	2.90	6.40		105.50	3.20	6.30	
71.20	3.50		10.90	108.70	3.10		
				111.80	2.70	4.90	8.10
20	3.20			114.50	2.20		
3.40	3.50	6.70		116.70	2.60	5.90	
6.90	3.50		9.50	119.30	3.30		9.00
10.40	3.90	7.40		122.60	2.90	6.20	
14.30	3.70			125.50	3.30		
18.00	2.20	5.90	9.50	128.80	2.80	4.70	6.90
20.20	3.60			131.60			
23.80	2.60	6.20					
26.40	3.30		8.00	70	1.90	5.00	
29.70	3.60	6.90		2.60	2.90		
33.30	2.30			5.50	2.10	6.00	8.20
35.60	2.80	5.10	9.80	7.60	2.70		
38.40	2.60			10.30	3.30	5.00	
41.00	2.60	5.20		13.60	2.20		9.20
43.60	3.90		10.20	15.80	2.80	6.40	
47.50	3.30	7.20		18.60	3.00		
50.80	2.60			21.60	3.40	6.70	9.00
53.40	3.20	5.80	8.70	25.00	2.80		
56.60	3.10			27.80	3.90		
59.70	3.90	7.00		31.70	3.30	6.30	10.30
63.60	3.10		8.90	35.00	3.00		

TABLE I.—*Continued.*

Time.	1 Division.	2 Division.	3 Division.	Time.	1 Division.	2 Division.	3 Division.
66.70	3.50	5.60		38.00	3.80	6.10	
70.20	2.10			41.80	2.30	6.90	9.60
72.30		6.00		44.10	4.20		
			9.90	48.30	2.70		
30	3.90			51.00	2.80	6.90	
4.20	2.40			53.80	4.10		10.80
6.60	2.60	5.00	8.40	57.90	4.50	71.0	
9.20	2.80	6.00		62.40	2.60		
12.00	3.20			65.00	3.70	6.40	7.60
15.20	3.90	7.00	8.60	68.70	2.70		
19.10	3.60			71.40	2.20	4.90	
22.20	2.20	5.30		73.60	2.70		
24.40	3.10		7.20	76.30			
27.50	2.80	6.20					
30.30	3.40						
33.70	2.40	4.70					

variation from a constant it seems quite remarkable to think that an apparently haphazard set of numbers unite on the average according to such a definite law.

TABLE II.

Drop No. 1.

Pressure = 24.8 cm. Temperature = 18.8° C.

V = .00296 cm./sec. $a = 4.04 \times 10^{-5}$ cm. k = .611.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
$1 \times .00916$	3.92	3.587	2.661	.463	7.58	60.9	707
$2 \times .00916$	6.694	6.811	5.515	.648	10.81	61.9	355
$3 \times .00916$	9.276	10.052	8.444	.804	13.03	60.2	239

Weighted mean $N = 61.0 \times 10^{22}$.

TABLE III.

Drop. No. 2.

Pressure = 24.8 cm. Temperature = 18.8° C.

V = .002770 cm./sec. $a = 3.93 \times 10^{-5}$ cm. k = .604.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
$1 \times .00916$	3.306	3.945	2.893	.526	7.16	65.0	312
$2 \times .00916$	6.612	7.589	5.901	.844	9.00	51.6	150
$3 \times .00916$	10.926	9.057	9.057	.934	12.02	61.2	95

Weighted mean $N = 60.7 \times 10^{22}$.

TABLE IV.

Drop. No. 3.

Pressure = 31.7 cm. Temperature = 19.5° C.

V = .001465 cm./sec. $a = 2.79 \times 10^{-5}$ cm. k = .577.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
$1 \times .00918$	6.27	8.11	4.85	1.63	4.44	64.7	208
$2 \times .00918$	12.54	14.80	10.48	2.16	5.62	72.1	102
$3 \times .00918$	18.81	22.44	16.38	3.03	7.08	54.8	70

Weighted mean $N = 64.8 \times 10^{22}$.

TABLE V.

Drop. No. 4.

Pressure = 12.25 cm. Temperature = 20.0° C.

V = .00303 cm./sec. $a = 3.12 \times 10^{-5}$ cm. k = .348.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
$1 \times .00918$	3.033	3.834	2.401	.716	4.87	55.8	338
$2 \times .00918$	6.06	7.108	5.237	.936	7.47	65.8	168
$3 \times .00918$	9.09	10.41	7.97	1.220	8.47	56.5	111

Weighted mean $N = 58.8 \times 10^{22}$.

TABLE VI.

Drop. No. 5.

Pressure = 13.52 cm. Temperature = 19.3° C.

V = .00393 cm./sec. $a = 3.99 \times 10$ cm. k = .442.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
$1 \times .00914$	2.325	2.735	1.997	.369	7.19	58.2	1010
$2 \times .00914$	4.650	5.172	4.146	.516	10.22	58.9	508
$3 \times .00914$	6.975	7.57	6.32	.635	12.65	60.2	336

Weighted mean $N = 58.8 \times 10^{22}$.

TABLE VII.

Drop No. 6.

Pressure = 15.65 cm. Temperature = 18.6° C.

V = .00321 cm./sec. $a = 3.69 \times 10^{-5}$ cm. k = .460.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
$1 \times .00914$	2.844	3.410	3.410	.500	6.51	60.7	968
$2 \times .00914$	5.688	6.404	4.962	.721	8.97	57.8	481
$3 \times .00914$	8.532	9.450	7.700	.875	11.05	58.4	319

Weighted mean $N = 59.0 \times 10^{22}$.

TABLE VIII.

Drop No. 7.

Pressure = 19.4 cm. Temperature = 19.1° C.

V = .00332 cm./sec. $a = 4.11 \times 10^{-5}$ cm. k = .551.

b	t_g	$\dot{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
1 × .00918	2.77	3.19	2.40	.395	8.00	65.8	561
2 × .00918	5.54	6.15	5.00	.575	10.88	60.6	283
3 × .00918	8.31	9.14	7.67	.735	12.93	57.2	188
4 × .00918	11.08	11.80	10.36	.780	16.05	66.1	142
5 × .00918	13.85	14.87	13.00	.935	16.75	57.7	109
6 × .00918	16.62	17.77	15.73	1.020	18.40	58.0	94

Weighted mean $N = 62.2 \times 10^{22}$.

TABLE IX.

Drop No. 8.

Pressure = 12.25 cm. Temperature = 20.0° C.

V = .00313 cm./sec. $a = 3.21 \times 10^{-5}$ cm. k = .357

b	t_g	$\dot{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
1 × .00918	2.932	3.683	2.384	.650	5.24	59.5	696
2 × .00918	5.864	6.792	5.030	.881	7.66	63.4	364
3 × .00918	8.796	9.860	7.774	1.043	9.68	67.5	229
4 × .00918	11.728	13.04	10.39	1.326	10.04	54.5	180
5 × .00918	14.660	16.129	12.972	1.578	10.54	49.1	136
6 × .00918	17.592	19.15	16.05	1.55	12.98	60.8	108

Weighted mean $N = 60.1 \times 10^{22}$.

TABLE X.

Drop No. 9.

Pressure = 19.5 cm. Temperature = 20.2° C.

V = .002420 cm./sec. $a = 3.31 \times 10^{-5}$ cm. k = .482.

b	t_g	$\dot{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
1 × .00918	3.795	4.708	3.109	.800	5.44	59.6	733
2 × .00918	7.590	8.700	6.500	1.100	7.84	61.8	378
3 × .00918	11.385	12.637	10.093	1.272	10.15	68.9	243

Weighted mean $N = 61.8 \times 10^{22}$.

TABLE XI.

Drop No. 10.

Pressure = 13.34 cm. Temperature = 20.5° C.

V = .003302 cm./sec. a = 3.39 cm. k = .400.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
1 × .00918	2.78	3.347	2.282	.532	5.97	58.8	586
2 × .00918	5.56	6.308	4.770	.769	8.20	55.4	301
3 × .00918	8.34	9.303	7.507	.898	10.60	61.7	192

Weighted mean $N = 58.4 \times 10^{22}$.

TABLE XII.

Drop No. 11.

Pressure Temperature

V = .003207 cm./sec. $a = 3.41 \times 10^{-5}$ cm. k = .395.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$N \div 10^{22}$	No. Obs.
1 × .00918	2.862	3.496	2.336	.580	5.67	58.2	503
2 × .00918	5.724	6.604	4.962	.821	7.95	57.0	245
3 × .00918	8.586	9.596	7.614	.991	9.83	58.2	159

Weighted mean $N = 57.9 \times 10^{22}$.

TABLE XIII.

Drop No. 12.

Pressure = 24.29 cm. Temperature = 21.1° C.

V = .00251 cm./sec. $a = 3.63 \times 10^{-5}$ cm. k = .572.

b	t_g	$\overset{+}{t}_a$	$\bar{t}_a$	τ	z	$\frac{z}{\sqrt{t_g}}$	No. Obs.
1 × .00922	3.672	4.365	3.078	.6435	6.50	3.39	2056
2 × .00922	7.344	8.349	6.480	.9345	8.93	3.31	1028
3 × .00922	11.016	12.237	9.926	1.156	10.83	3.27	681
4 × .00922	14.688	15.999	13.333	1.333	12.48	3.24	514
5 × .00922	18.360	19.916	16.915	1.501	13.85	3.23	393
6 × .00922	22.032	23.423	20.387	1.513	16.44	3.50	342
7 × .00922	25.704	27.630	23.918	1.856	15.67	3.10	268
8 × .00922	29.376	30.981	27.309	1.831	18.12	3.34	252
9 × .00922	33.048	35.143	30.941	2.10	17.85	3.11	226
10 × .00922	36.720	38.92	34.73	2.09	19.86	3.28	190

Weighted mean $N = 60.0 \times 10^{22}$. Total No. Obs. = 5,950.

Table XIV. contains a summary of the 12 drops with the final weighted mean values of N which were obtained by assigning weights according to the number of observations that were taken. They are arranged in ascending values of l/a in order to show that N has no tendency to gradually increase or decrease, although k changes from .357 to .611. This is a verification that Millikan's expression for k is correct, at least for this region and for air.

TABLE XIV.

Drop No.	$a \times 10^4$	$z \times 10^4$	$1/a$	k	$N \div 10^{23}$	No. Obs.
4	3.12	5.75	1.840	.348	58.8	617
8	3.21	5.75	1.790	.357	60.1	1,713
10	3.39	5.30	1.562	.400	58.4	1,079
11	3.41	5.30	1.553	.395	57.9	907
5	3.99	5.19	1.300	.442	58.8	1,854
6	3.69	4.48	1.215	.460	59.5	1,768
9	3.31	3.61	.917	.482	61.8	1,354
7	4.11	3.62	.880	.551	62.2	1,377
12	3.64	2.91	.800	.572	60.0	5,950
3	2.79	2.22	.795	.577	63.8	380
2	3.93	2.83	.710	.604	59.3	557
1	4.04	2.83	.700	.611	61.0	1,281

Weighted mean = 60.0×10^{23}. Total No. Obs. = 18,837.

As indicated heretofore all of the above computations have been made on the assumption that $R = 82.9 \times 10^6$ and $\mu_{23} = .0001826$. Professor Millikan calls my attention to the fact that the correct value of R is 83.15×10^6 and that the most probable value of μ_{23} is .0001824.[1] The introduction of these changes increases the above value of N by .41 per cent. The probable error computed on the ordinary way from column 6 of Table XIV. is $.3 \times 10^{22}$ or .5 per cent. This represents the "probable error" in the z^2 term of equation 10. The *uncertainty* in this term, the mean being obtained from but 12 numbers, is of course considerably larger. Professor Millikan estimates the uncertainty in his determination of the k term of (10) [more accurately the ak term, since this is the quantity actually given by his experiments] for these values of l/a, at about 1 per cent. So that we may consider that the uncertainty in the above determination of N by the Brownian movement method does not exceed 2 per cent. The value actually obtained, viz., 60.3×10^{22} differs by but .5 per cent from the value obtained by Professor Millikan, namely, 60.62×10^{22}.

The results of this investigation show then that the number of molecules in a gram molecule of air is

$$N = 60.3 \times 10^{22} \pm 1.2 \times 10^{22}.$$

In conclusion I wish to express my indebtedness to Mr. Carl F. Eyring, who has assisted me in taking a large portion of the observations and in computing the average values.

PHYSICAL LABORATORY,
BRIGHAM YOUNG UNIVERSITY,
July 17, 1914.

[1] Ann. d. Phys., 41, p. 759, 1913.

COLOR ANALYSES OF TWO COMPONENT MIXTURES.[1]

BY L. A. JONES.

IT is a well-known fact in physiological optics that if two or more colors are viewed in rapid succession the resultant sensation will be a color which is a mixture of the colors so viewed. For instance, if a disk of which one half is red and the other green be rotated rapidly, the entire disk will appear to be yellow. This mixing is due to what is known as the persistence of vision; that is, the sensation produced by a given stimulus continues to exist for a short period of time after the stimulus has ceased to act.

Now if we have a white screen illuminated by white light from a projection apparatus and in the path of the light is placed a rapidly rotating disk composed of two or more light filters such as colored glass or dyed gelatine film, the screen will appear to be illuminated by light of a color which is a mixture of the colors in the rotating disk. In case the disk is made up of two filters that in color are exactly complementary and if the densities of the filters and the sizes of the sectors are in the proper ratio to each other, the screen will appear white, just as with no disk in the path of the illuminating beam. When this condition is altered in any way, either by changing the colors of the sector so that they are no longer complementary, or by altering the relative sizes or densities of the filters, the screen will appear to be illuminated by light the color of which will depend upon the way in which the disk has been altered. The work of which this paper is a report was carried out in order to determine definitely the hue and purity of all the colors that it is possible to produce in this way with a given pair of color filters. The method used was to produce by means of an adjustable rotating disk made up of the filters to be examined all possible combinations and to analyze the resulting colors with a colorimeter of the monochromatic type.

A diagram of the disk used for producing the mixtures is shown in Fig. 1. Two disks of brass were cut as shown at *a*, Fig. 1. The openings AA' BB' were each 80° in angle, the metal strips between the openings being each 10°. These two disks could be rigidly fastened together by placing the small nuts, *N*, on screws projecting from one of the disks through holes in the other. The filter film was placed between these disks so as to

[1] Communication No. 11 from the Research Laboratory of the Eastman Kodak Company.

cover the openings and when the screws were tightened was held so rigidly that the disks could be rotated very rapidly without displacing the filters.

A third disk was cut as shown at *B*, Fig. 1, the angles of the openings *CC'* each being 90°. This disk was placed with the two carrying the filters upon the shaft of a small motor and secured in position with a collar and nut.

A scale was laid off on one of the disks as shown in *a*, and one index line, *I*, on the other, *b*. When the index was set at 0 on the scale, the openings *BB'* were completely covered and the ones *AA'* fully open. Now it will be seen that if the openings *AA'* was filled with a filter of one color, and *BB'* with some other, that by moving the index along the scale from 0 to 1.0 all possible combinations of the two filters were obtained. The composition of the mixture produced by the disk was computed as follows:

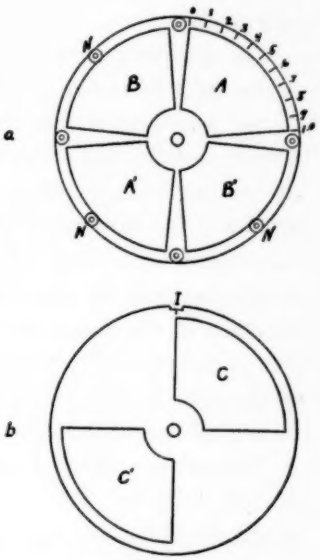

Fig. 1.

Let *S* the setting of the index line on the scale,

Ta the transmission of the filter in openings *AA'*,

Tb the transmission of the filter in *BB'*,

A the ratio of the intensity of the light through the *AA'* filters to the intensity of the mixture produced (in per cent.),

B ratio of the intensity of the light through the *BB'* filters to the intensity of the mixture produced (in per cent.).

$$B = \frac{S \cdot T_b \cdot 100}{S \cdot T_b + (1 - S)Ta} = 100 - A,$$

$$A = \frac{(1 - S)Ta \cdot 100}{S \cdot T_b + (1 - S)Ta} = 100 - B.$$

The mixtures produced were analyzed with a colorimeter of the monochromatic type as designed by P. G. Nutting,[1] and built by Adam Hilger of London. The principle involved in making an analysis of a color with this instrument is that any color can be matched, as far as the visual sensation is concerned, by mixing a pure spectral light of some definite wave length with the proper amount of white light. The only

[1] P. G. Nutting, Zeit. Instrumentenjunde, Vol. 33, p. 20, Jan., 1913.

exception to this rule is in case the unknown color is a purple, that is, some mixture of red and blue, and in that case if the proper amount of a pure spectral hue be mixed with the unknown a sensation white will be produced.

The spectral hue with which standard white must be mixed to match a given color is known as the dominant hue of the color and the intensity of the standard white expressed as a percentage of the sum of the intensities of the hue and white added together to match the color is known as the per cent. white of the color. Any color then can be accurately analyzed by this method in terms of the wave-length of the dominant hue and the per cent white. In case the color is a purple the terms in which the analysis must be expressed are the wave length of the complementary of the dominant hue and the per cent. hue. The term per cent. hue is defined as the intensity of the pure hue expressed as a percentage of the sum of the intensities of that pure hue and the unknown that must be added together to produce sensation white.

This method of color analysis involves the establishment of a standard of white light. The most logical definition of this is that standard white shall be direct sunlight near noon of a clear day. A large number of measurements extending over a considerable period of time show that the light as above specified is constant in color,—no measurable variations having been observed.

For a complete specification of a color one other factor must be taken into consideration. This third term may be said to be the intensity factor, being for a source the intensity of the light emitted, for a transmitting screen the transmission, and for a reflecting surface the reflecting power. The measurement of this term involves other methods and other apparatus than the colorimeter as used in this work. The nature of a color is by this method of analysis expressed by two terms, the wave length of the dominant hue and the per cent. white, the measurement of which depends in no way upon arbitrary, non-reproducible standards such as are frequently used in colorimeters of other types.

In Fig. 2 is given a diagram showing the arrangement of the essential parts of the instrument. The body of the instrument, *O*, is a rectangular metal box which serves as a triple collimator. On one end of this are attached three metal tubes in each of which is placed a pair of nicol prisms. One prism of each pair is fixed in position and the others can be rotated by means of an attached graduated quadrant which moves past a fixed index line, thus the intensity of the light transmitted by each pair can be changed at will, and by reading the scales the ratio of the incident to the transmitted intensities can be determined for each

pair. At the other end of box O are placed the three collimating lenses, L_1, L_2, L_3. P is a dispersing prism of the constant deviation type actuated by a screw which carries the drum, D, graduated so as to read directly

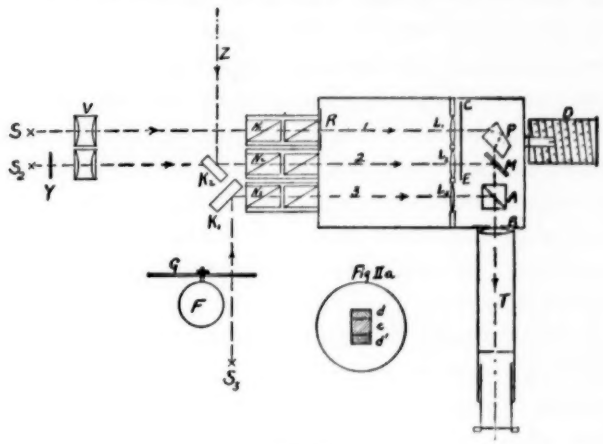

Fig. 2.

in wave-lengths. M is a plane parallel plate of colorless optical glass set so as to reflect a part of the light coming through N_2L_2 along the axis of the observing telescope, T. A is a Lummer-Brodhun cube of special design, the diagonal faces being so ground that the field as seen through the rectangular diaphragm, B, of the observing telescope is as shown in Fig. 2*a*. The portions of the field, d, d', are illuminated by the light which comes through N_3L_3 and is totally reflected at the diagonal face of cube A, while the central part of the field, c, is illuminated by light which comes through collimators 1 or 2, or by a mixture of the two beams, and is transmitted by the cube A, where the diagonal faces are in optical contact.

This particular type of field is extremely well adapted for use in this instrument. In making a setting the color of field c is to be matched with the color of the fields dd'. Suppose that the attention is fixed on the dividing line between c and d, and that the adjustments are made so that there is a just perceptible color difference between fields c and d. Now if the attention be shifted to the line between c and d', the lack of color match will appear much greater than before. This is due to fatigue and the existence of after image in the retina of the observer's eye. By taking advantage of this effect and shifting the attention from one dividing line to the other while making a setting, the color match can be made with greater precision than with other types of fields.

The observing telescope is provided with a pin-hole ocular, the diameter

of the opening being about 1.5 mm. The focal lengths of the lenses and the dimensions of the instrument are such that if an image of a light source is formed on the slit, R, the central portion of the field c, will be illuminated by monochromatic light, the wave-length of which can be adjusted to any desired value by rotation of the drum, D.

Now if white light is admitted through N_2, it will be mixed with the light of pure hue at M and the field c will be illuminated by this mixture. The ratio of the intensities of the two beams thus mixed can be given any desired value by rotating the movable prisms in N_1 and N_2, and the value of the ratio determined by reading the attached scales. The light of unknown color that is to be analyzed is admitted through N_3 and illuminates the field dd'. The intensity of this beam can be changed by rotating the nicol in N_3.

At CE is a thin metal plate used when making the per cent. white determination, which is so attached to the frame of the instrument that it can be raised out of the field while the color match is being made and lowered into position when it is desired to make the per cent. white reading. This plate is of such shape that when in position it cuts off the lower half of the beam coming through L_1, and the upper half of that coming through L_2. In this way the upper half of the field c, Fig. 2*a*, is illuminated by light from N_1L_1, and the lower half by that from N_2L_2. Then by adjusting the movable nicols in N_1 and N_2 a photometric balance between the two halves of field c can be obtained and the ratio between the intensities of the pure hue and the white of a given mixture can be determined.

The measurement of the third term necessary for the complete specification of a color involves the use of some form of photometer. In this work the transmissions of the color filters used were measured on a 12-foot bench photometer equipped with a Martens flicker photometer head. The difficulties in measuring the transmission of a colored filter are the same as those which occur in the photometry of colored lights. It has been shown by Ives and others that the flicker method gives the most reliable results in heterochromatic photometry and hence this method was adopted as being best suited for the determination of the transmissions of the filters used in this investigation. The transmissions were determined for the light of the carbon arc which was also used in producing the color mixture.

The arrangement of the colorimeter as used in this work is shown in Fig. 2. S is a Nernst glower, one image of which is formed by the condenser V upon the slit R. A beam of sunlight Z, was thrown by means of a heliostat upon a block of magnesium carbonate, K_2, in front of N_2.

This was the source of the standard white light used when possible. On cloudy days a Nernst glower, $S2$, screened by a blue filter, Y, to match standard white was used as a source of white light. Several series of measurements were made with both sunlight and the screened glower as the source of standard white and in all cases the differences were so small as to be negligible, being less than the variations liable to occur due to differences in the filter film.

The color to be analyzed was produced by projecting a beam of light from a direct current carbon arc, $S3$, through the mixing disk, G, which was rotated at high speed by the motor, F, on the block of magnesium carbonate, K_1, placed in front of N_3. The arc used was an automatic Weuler with 7 mm. carbons taking a current of about 8 amperes The carbon arc is almost always used in practical work as a light source for projection, and as it was desired to imitate practical conditions as nearly as possible the arc was used instead of standard white light which should be used in case the problem is one involving only a high precision analysis of a colored transmitting screen or reflecting surface.

In making the analysis of a given mixture the intensities of the three beams of light 1, 2, and 3 were adjusted by rotating the prisms in N_1, N_2, and N_3, and the wave length of the pure hue was varied by turning D until the field C exactly matched the fields dd' in color and intensity. (It is very important that an intensity match be maintained in order that the color match may be made with precision.)

When a satisfactory match was obtained the wave length of the dominant hue was read from the drum D, and the reading, D_h, of the scale attached to the movable nicol in N was recorded. Then the metal plate CE was dropped into position, the light coming through N_3L_3 cut off, and without changing the setting of the scale on N_2 a photometric balance was made between beams 1 and 2 by rotating the nicol in N_1, and the reading, D_u, of the attached scale recorded. From the readings thus obtained, *i. e.*, D_H and D_u the per cent. white was computed.

TABLE I.

No.	Approx. Color.	Hue ($\mu\mu$).	% W	Tr (%)
22	Orange Red	604.5	3.0	47
25	Red	624.0	3.3	24
44	Blue Green	497	28.0	16
59	Green	547	13.0	22
60	Green	527	27.5	24
94	Red	615	4.0	30
IX	Blue Green	506	61.0	58
2–(IX)	Blue Green	502	53.0	40
4–(IX)	Blue Green	498	46.5	24

The filters used were standard Wratten light filters of dyed gelatine and are designated by catalog number.[1] In Table I. are given the color analyses of the filters used in this investigation.

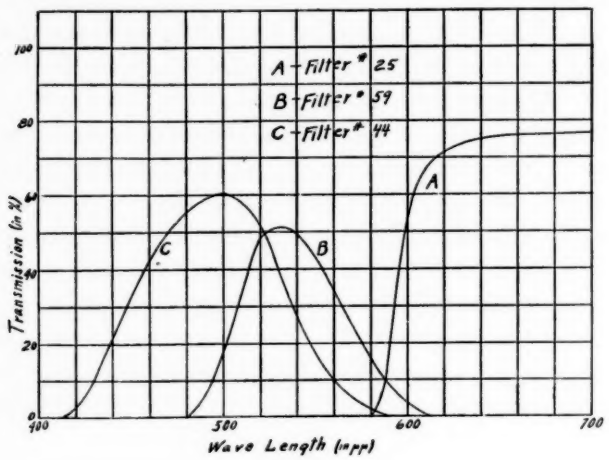

Fig. 3.

In Figs. 3, 4 and 5 are given the spectrophotometric curves of the filters used. The measurements were made with a spectrophotometer of the Hüfner type built by Hilger. The results are plotted with the transmission in per cent. as ordinates, and the wave lengths in — as abscissæ.

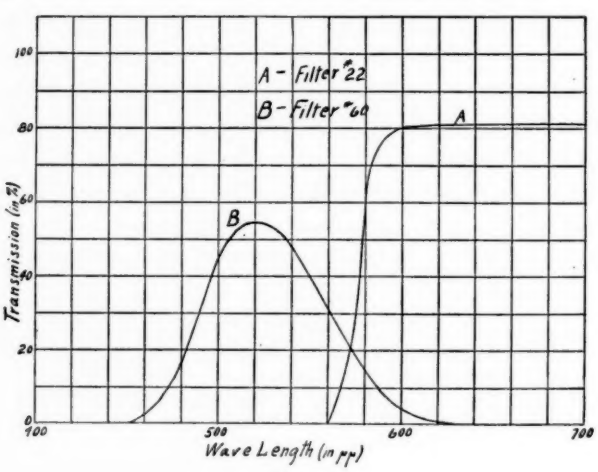

Fig. 4.

The values of the transmission are subject to a probable error of about 2 per cent.

[1] Atlas of Absorption Spectra, by C. E. Kenneth Mees.

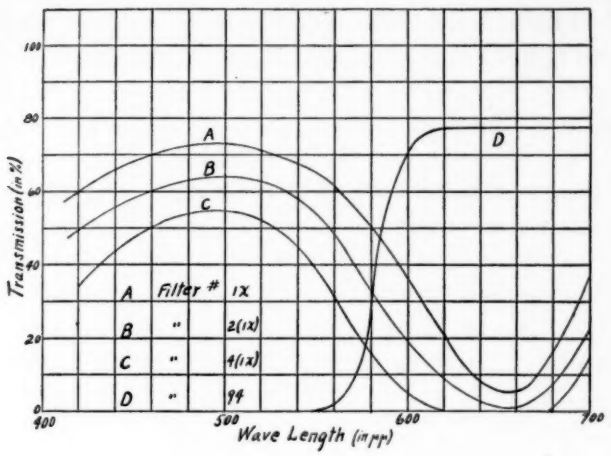

Fig. 5.

In making the color analyses of the mixtures the pair of filters to be used were placed in the disk as previously described and a set of readings taken at successive points from 0 to 1.0 on the scale. This procedure was repeated two to five times on each pair of filters. After computing the readings for each run the mean of all the results for a given scale setting was taken and the results plotted.

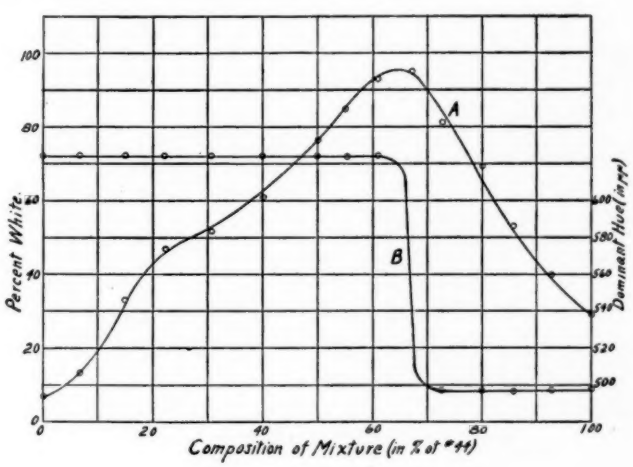

Fig. 6.

In Table II. is given a typical set of measurements including three complete runs made on one pair of filters. This is given to show the agreement of the analyses obtained in the runs made on different days. Runs No. 1 and No. 2 were made with the screened glower as a source of

standard white light, No. 3 with sunlight. It will be seen that the agreement obtained is quite good, and that the screened glower answers very well as a source of standard white for work of this kind.

The means of the measurements on this pair of filters, No. 44 and No. 25, are plotted as curves in Fig. 6. The abscissæ are the composition of the mixture expressed in per cent. of filter No. 44. The ordinates on the left are per cent. white referring to curve *A*, those on the right being wavelength of the dominant hue (in $\mu\mu$) referrring to curve *B*. The values of the ordinates of the two curves at per cent. No. 44 0 give the color analysis of the filter No. 25, and at per cent. No. 44 100 the analysis of No. 44. The analysis of any mixture of the two is given by the ordinates of the two curves at the abscissa value representing the given composition.

TABLE II.

Comp. of Mixture.			Dominant Hue ($\mu\mu$).				Per Cent. White.			
S	Per Cent. No. 44.	Per Cent. No. 25.	Run No. 1.	No. 2.	No. 3.	Mean.	Run No. 1.	No. 2.	No. 3.	Mean.
0.00	0	100	624	624	623	623.6	2.4	4.2	3.6	3.4
0.10	6.9	93.1	624	624	623	623.6	12.8	12.0	15.3	13.4
.20	14.3	867	624	623	622	6230	33.8	29.7	31.7	31.7
.30	22.2	77.8	624	624	623	623.6	43.6	47.4	47.9	46.3
.40	30.8	69.2	624	624	623	623.6	51.4	53.8	48.0	51.1
.50	40	60	624	623	623	623.0	61.1	66.9	57.4	61.8
.60	50	50	623	23	22	622.6	76.8	75.2	77.7	76.6
.65	55.3	447	624	22	22	622.6	83.8	81.8	88.2	84.8
.70	60.8	392	630	22	22	6216	92.2	92.7	95.0	93.3
.75	66.7	333	—	—	—	——	96.2	94.2	92.3	94.6
.80	72.7	273	497	498	498	497.6	80.7	80.5	80.0	80.7
.85	79.1	208	497	497	498	497.3	69.8	69.9	68.8	69.5
.90	85.7	14.3	498	497	499	498.0	54.4	54.8	50.6	53.3
.95	92.8	7.2	498	497	498	497.6		—	40.6	40.6
1.00	100	0	498	497	497	497.3	29.1	27.1	28.5	28.2

It will be seen from these curves, that as light though No. 44 was added in increasing amount to the light transmitted by No. 25, that the resultant mixture increased in per cent. white to a max. of about 95 per cent. at per cent. No. 44 65 and then decreased. The dominant hue of the mixture did not change until the per cent. white had reached a maximum and then it shifted suddenly from the dominant hue to filter No. 25 to that of filter No. 44. Thus with this pair of filters it was possible to obtain colors of only *two* dominant hues, but the per cent. white varied from that of the separate filters to 95 per cent. At the point per cent. No. 44 65 the mixture was so near white that the dominant hue was indeterminate, in fact, any color having 95 per cent. white shows a barely perceptible differ-

ence from pure white. These filters then are very nearly complementary to each other. That is the light transmitted by them when mixed in proper ratio produces very nearly a sensation white.

The results obtained with the other filters are given in the form of curves, Figs. 7 to 12, plotted as in Fig. 6. Each point plotted represents the mean of several determinations. The variations in the separate readings taken at a given point were of the same order as those shown in Table II.

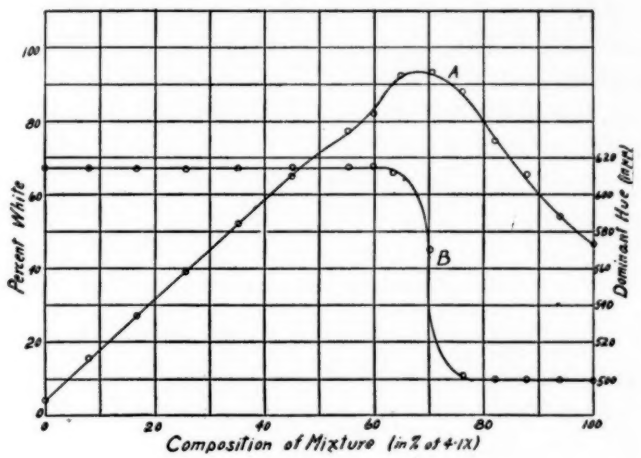

Fig. 7.

In Fig. 7 are given the analyses of the mixtures produced with filters No. 94 and No. IX. Four thicknesses of No. IX were used against one of No. 94. The maximum per cent. white was 94. This combination is very nearly complementary, but not so closely so as the pair used in Fig. 6.

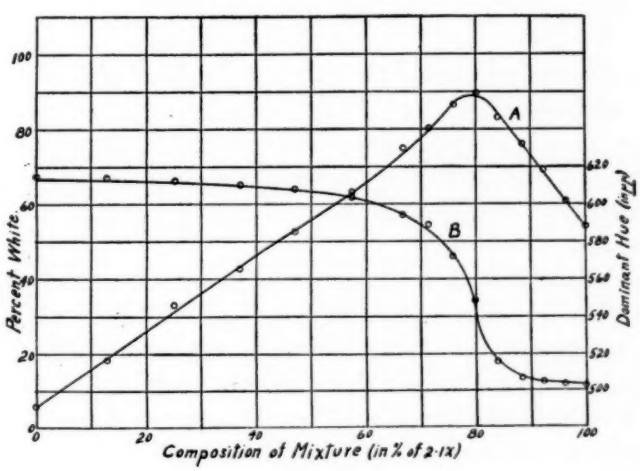

Fig. 8.

Here again the entire range of mixtures produced colors of only two hues, but a wide variation in purity. The change from one hue to the other was very sudden and occurred at the point of maximum per cent. white.

In Fig. 8 the analyses were obtained by using two thicknesses of No. IX. against one of No. 94. Here the maximum per cent. white obtained was 90, and the per cent. white curve, *A*, not so flat on top as in Fig. 6. That is, the range of mixtures that give high per cent. white values was less than with filters that are more nearly complementary. It will be noted also that the change in hue was more gradual, but that here again, the maximum rate of change in hue was at the point of maximum per cent. white. With this pair then colors of all hues from 504 $\mu\mu$ to 615 $\mu\mu$ could be produced, but in the region of hue 550 $\mu\mu$ the colors were very dilute; that is, of high per cent. white.

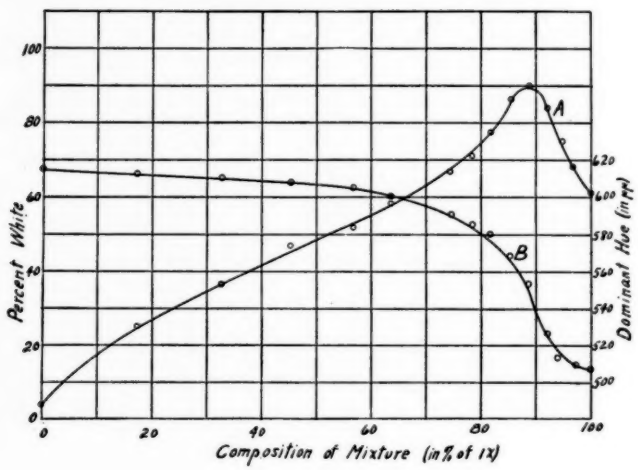

Fig. 9.

In Fig. 9 the analyses are of the mixture obtained with one thickness of No. IX, with one of No. 94. Here the region of high per cent. white was narrower than in any of the preceding cases, the maximum value being 90 per cent. The change in hue was more gradual than before, but again the maximum rate of change in hue was at the position of maximum per cent. white.

It will be noted that in the last three cases discussed, the same red component, No. 94, was used with one, two and four thicknesses of No. IX. As the number of thicknesses used was increased, the total transmission and the per cent. white of the resulting filter decreased, and the wave length of the dominant hue shifted (see Table I.). These changes were accompanied by the changes in the color analyses curves previously referred to in the discussion of Figs. 7, 8, and 9.

In Fig. 10 are given the results obtained with filters No. 22 and No. 60. In this case the filters were far from being complementary, and no mixture produced a color of high per cent. white. The hue curve is almost a

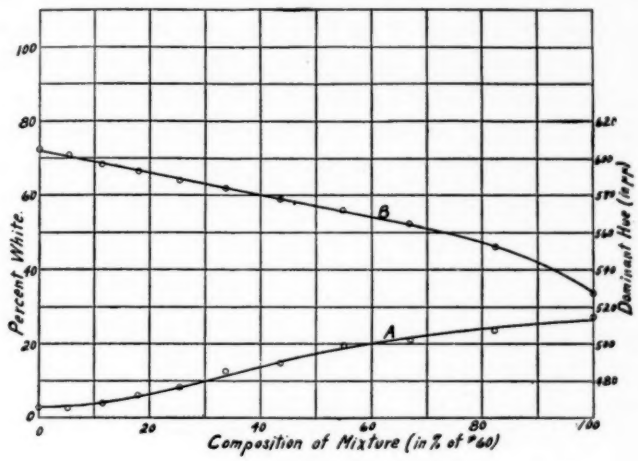

Fig. 10.

straight line, as is also the per cent. white curve. With this pair colors of all hues between those of the component filters were produced, and the per cent. white was always less than that of the green component No. 60.

In Fig. 11 the curves show the analyses obtained with filters No. 25 and No. 59. Both curves are straight lines to within the possible errors of measurement. The changes in hue and per cent. white were uniform throughout the entire range. The highest per cent. white was that of the

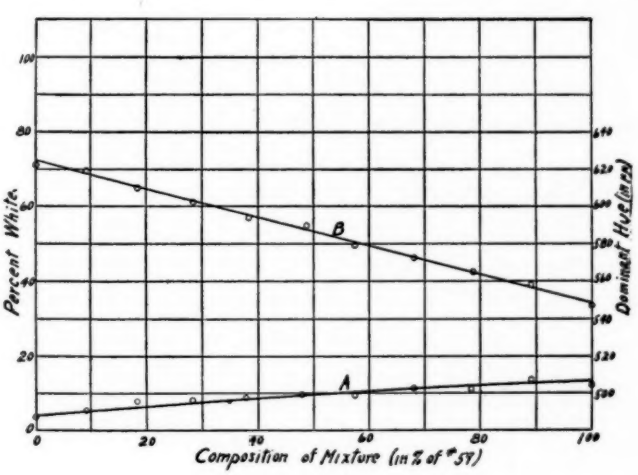

Fig. 11.

green component itself. With this pair colors of all hues between those of the two components were produced.

Conclusions.—The conclusions to be drawn from the results are:

It is not possible with two filters that are complementary or nearly so to produce mixtures that show appreciable color of more than two dominant hues, those hues being the dominant hues of the filters themselves.

With a pair of filters of the tri-color type such as No. 25 and No. 59 it is possible to produce mixtures having low per cent. white values and of all hues lying between the dominant hues of the filters themselves but no mixture can be produced with such a pair that has a high per cent. white value.

This method of analysis affords a very good means of showing how closely any two filters approach the condition of being complementary to each other. The per cent. white curve, in case the filters are exactly complementary, must reach a maximum of 100 per cent. and at the abscissa value corresponding to this maximum the hue curve must change abruptly from the dominant hue of one of the components to that of the other.

The results given are confined to mixtures produced by red and orange red with blue and blue green. A large amount of work remains to be done with other colors, and the author hopes at some time to do something further along this line.

The author wishes at this time to thank Mr. F. A. Elliot for his valuable aid in the computing of data and in the plotting of the results presented in this paper.

THE INFLUENCE OF ANNEALING ON THE CHARACTERISTICS OF LIGHT-SENSITIVE SELENIUM.

By E. O. Dieterich.

AN extension, by Brown and Sieg,[1] of the work of Pfund in analyzing selenium cells by means of the spectrum revealed the fact that, classified according to their wave-length sensibility curves, a great number of different types of selenium cells were possible. Previous investigations by Pfund,[2] Stebbins,[3] Brown and Sieg,[4] and Nicholson[5] pointed to the conclusion that a typical wave-length sensibility curve existed which was essentially the same for all selenium cells, for, in all cases recorded, a maximum in the red end of the spectrum was found. The cells investigated were, in general, made by either Giltay or Ruhmer. The process of making these is a trade secret, but it is quite likely that the same method of crystallization is followed in all the cells of either one of the above types. Pfund, in his earlier experiments, used some cells of his own construction; these, too, were all crystallized in the same manner.

In some later experiments by Brown and Sieg, cells prepared by the author were used. Sensibility curves were obtained which differed widely, some showing a maximum in the red, some having hardly any sensitiveness in the red but a maximum in the blue. An analysis of the data covering the method of construction of these revealed the fact that the crystallization of the selenium took place under different conditions in the different samples. This immediately suggested the possibility that a better knowledge of the conditions governing the construction of light sensitive selenium cells might be of assistance in explaining the action of light sensitive selenium. With this purpose in view, the investigation summarized in this paper was carried out.

This paper will describe the method followed in making the cells, and will show that the resistance and the shape of the wave-length sensibility curves of selenium cells can be controlled by varying the process of annealing. A simple explanation for the different types resulting will also be offered.

[1] Phys. Rev., Series 2, IV. p., 48, 1914.
[2] Phys. Rev., XXVIII., p. 324, 1909; XXXIV., p. 370, 1912; Phil. Mag., VII., p. 26, 1904.
[3] Astrophys. Jour., XXVII, p. 183.
[4] Phys. Rev., Series 2, II., p. 487, 1913.
[5] Phys. Rev., Series 2, III., p. 1, 1914.

METHOD OF MAKING.

The cells, of which about 40 were constructed for this investigation, were all of the Bidwell type, *i. e.*, two parallel wires were wound spirally around an insulating form and the spaces between the wires filled with selenium.

The selenium used was some in stick form from Merck. No steps were taken to further purify it, since it is, according to other observers, quite pure. Moreover, Pfund[1] has shown that the presence of metallic selenides does not affect the shape of the wave-length sensibility curve. In a few samples made, rather impure selenium was used, and the cells resulting were not as satisfactory as those made with selenium from Merck. The resistance of these was, in general, very high, and they were sluggish in action although they had essentially the same characteristics as those made from the purer element. Marc[2] has observed that impure selenium crystallizes less completely in a given time than pure selenium. To this fact the unsatisfactory action of the samples made with impure selenium is ascribed.

As insulating material soapstone was used. At first, glazed porcelain was tried, but it proved unsatisfactory on account of the difficulty of working into forms. The advantages of the talc over the porcelain are evident. It is just as efficient as an insulator, besides being much softer, and, therefore, capable of being easily machined.

Several kinds of wire were tried as electrodes, copper, nickel, platinum, German silver, and Advance wire. Again although selenides are formed during the crystallization process, due to the high temperature, the shape of the wave-length sensibility curve will not be changed, although the sensitiveness and the resistance of the cell will be affected. These points are to be verified in some later work. Copper, German silver and Advance wires have this disadvantage that, at the temperature of annealing, a film of oxide covering the wire is readily formed. This so materially increases the resistance of the cell as to make it practically useless for investigation except with very sensitive apparatus. Nickel wire is much less easily oxidized and proved as satisfactory as platinum wire, besides being less expensive, and was used in all except the first few cells.

The size of the sensitive surface was about 1×3 cm., except in the first few cells which were larger. The distance between the electrodes was a little less than 1 mm.

In applying the selenium to the form the following method was

[1] Phil. Mag., VII, p. 26, 1904.

[2] Marc, Die Physikalisch-Chemischen Eigenschaften des metallischen Selens, 1907.

adopted as being the most satisfactory. The form was heated, on a hot plate, to a temperature just above the melting point of selenium, 217° C., and then the selenium, in stick form, was rubbed over the heated surface immediately on removing from the hot plate. As is well known, with this treatment, the selenium at once changes, on solidification, to the gray metallic variety and is conducting and light sensitive. By this method smooth, thin films of selenium were obtained. However, in all cases in which the samples were tested out immediately on making, the resistance was found to be very high, of the order of 10^8 ohms, and the sensitiveness, even under intense illumination, in no case greater than 5 to 1. (By sensitiveness is meant the ratio of the resistance of the cell in the dark to that in the light.) Upon making, therefore, the cells were "annealed," the process taking place in an electric oven whose temperature could be quite accurately controlled. It is in this "annealing" process, which consists merely in keeping the cells for some time at a high temperature, or in gradually changing the temperature, that the changes which impart different characteristics to the cells take place. This will be described in greater detail in a later section since it is varied from cell to cell.

In general, all the samples received the same treatment after annealing. They were allowed to come to a temperature of 170° C. while in the oven, then removed and placed in small glass tubes which had been thoroughly cleaned and dried. They were then sealed to prevent the access of moisture and other vapors, and allowed to come to room temperature. Usually they were allowed to rest for 24 hours before being investigated, being kept in a light-tight box in the meanwhile. With these precautions, all the samples were found to be permanent, with respect to light sensitiveness, at least throughout this investigation.

At first, the method generally described for crystallizing the selenium namely, heating it for a few minutes at about 180° C., was followed. The first cell made in this way had a high sensibility but was not permanent. The next few samples were not at all satisfactory, so the method was abandoned. Instead, the cells were annealed at higher temperatures and a longer time was taken for the process. By this method samples were obtained which were quite satisfactory in respect to sensitiveness.

Characteristics of the Cells.

The cells were investigated with respect to resistance, sensitiveness, shape of wave-length sensibility curve and permanence.

Resistance.

The resistance of the cells was measured by means of a Wheatstone bridge. Since the resistance varies with the voltage impressed upon it, the same E.M.F., 16 volts, was used throughout.

Here the observations of Ries[1] in regard to the variation of resistance with annealing were verified. Thus Ries records two samples which were heated at different temperatures, and shows that the higher the temperature to which the cell was heated the lower was its resistance. His method differs from that employed in this investigation, however, in that he subjected the individual cells to a series of temperature changes, alternately heating and cooling each cell, and measuring its resistance and sensitiveness while it was at room temperature. In these experiments each cell was subjected to a high temperature but once, but the results were the same as those obtained by Ries. The following table gives some typical data.

TABLE I.

No. of Cell.	Temp. of Annealing.	Period of Annealing, Hrs.	Resistance, Ohms.
23	210–200° C.	6	233,000
22	210° C.	4	358,000
28	210° C.	5	490,000
16	180° C.	3½	1,400,000
15	190° C.	2	3,690,000

From the above table the influence of annealing on the resistance of the cells can be clearly seen, namely, that the higher the temperature of annealing and the longer the time, the lower is the resistance.

It was further found that if the cells were heated for a short time only at a high temperature and the annealing carried on to completion at a lower temperature the resistance of the cells was materially reduced. This fact is shown in Table II. Thus, cells No. 18 and 19 were given

TABLE II.

Cell.	Temp. of Annealing.	Period of Annealing, Hrs.	Resistance, Ohms.
18	210° C.	½	976,000
	180° C.	9	
19	180° C.	9	40,000,000
20	210° C.	½	250,900
	180° C.	14	
21	180° C.	14	9,500,000

[1] Ries, Das elektrische Verhalten des Kristallinischen Selens gegen Wärme und Licht, 1902.

exactly the same treatment except that cell No. 18 was given a preliminary heating of half an hour at 210° C. The resistance of No. 18 is seen to be less than 1/40 that of No. 19. The same is true of No. 20 and 21.

The resistance of the freshly made cells was, in general, low, but increased gradually, reaching a constant value in a few weeks after making. This gradual, permanent increase is no doubt due to the contraction of the selenium and its consequent tearing away from the electrodes. The resistance of the various samples ranged from 12,000 ohms to 42,000,000 ohms.

Light-Sensitiveness.

With regard to the effect of annealing on the sensitiveness of the cells not much can be said as a result of these experiments. Two cells of remarkably high sensitiveness were obtained, but this was not permanent, the sensitiveness decreasing to about 1/5 of the original value in less than one month. That phase of the subject is under investigation at the present time, nothing definite having been discovered thus far, however. The sensitiveness of the samples, with the exception of the two mentioned above, varied between 5/1 and 20/1, using a 16 c.p. light at a distance of 30 cm. as a source of illumination.

The Wave-Length Sensibility Curves.

In order to determine the wave-length sensibility curves, the same method of procedure as outlined by Brown and Sieg[1] was followed and the same apparatus was used. Three periods of exposure of the cell to light were used; .4 sec., 10 sec., and 30 sec., the time of exposure depending upon the resistance of the cell. The range, in general, was from 460 $\mu\mu$ to 800 $\mu\mu$, since at values lower than 460 $\mu\mu$ the energy of the source was not great enough to measure very accurately. The exposure always took place in the order from short to long wave-lengths, since Brown and Sieg have shown that the order of exposure does not affect the shape of the curve. The slit width and other factors were kept constant throughout the investigation.

It was found that, except in a few cases, the shape of the wave-length sensibility curve did not change, whether the intensity of the incident light were high or low, or whether the time of exposure were long or short. This is shown by the curves for cell No. 10 in Fig. 1. Here the wave-lengths are plotted as abscissæ, and the change in resistance, which is proportional to the deflection of the galvanometer, as ordinates.

[1] Loc. cit.

It is seen from Fig. 1 that the curves for cells of the type represented by No. 10 do not change in their essential characteristics when the energy of the incident light is varied by as great a factor as 50, nor when the time of exposure changes from .4 sec. to 30 sec. Whenever possible, therefore, on account of the sensitiveness of the apparatus, the exposures were made for .4 sec. Cell 17, Fig. 1, represents the type in which a change in the energy of the incident light changes the shape of the curve. These are the typical curves obtained by other observers for the Giltay type of cells.

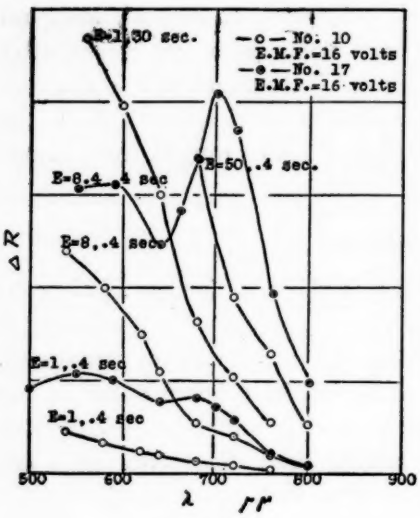

Fig. 1.

A wide variety of types of sensibility curves resulted, maxima being obtained at points not previously recorded. Fig. 2 shows the location of some of the most pronounced maxima developed in this investigation. These curves are not plotted to the same scale and, hence, do not show the relative sensibility of the cells; neither do they represent all the

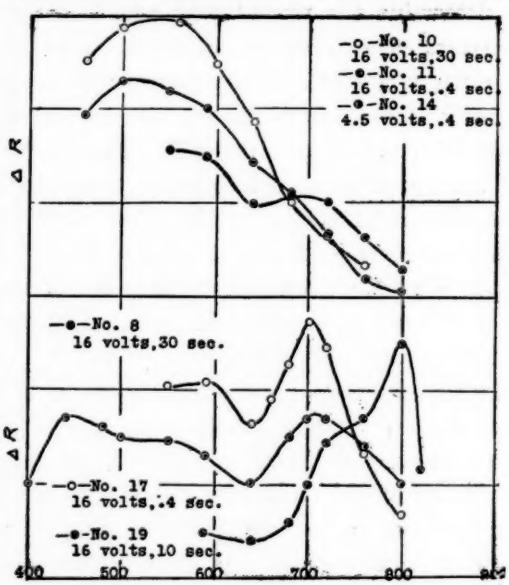

Fig. 2.

types possible to obtain. At the following wave lengths definite maxima were found: 440 $\mu\mu$, 500 $\mu\mu$, 550 $\mu\mu$, 700 $\mu\mu$, 720 $\mu\mu$ and 800 $\mu\mu$.

From Fig. 2 it is seen that the cells can be divided, in general, into two groups, viz., those that have their maximum sensibility at wave-lengths greater than 640 $\mu\mu$, and those in which the maximum occurs at wave-lengths shorter than 640 $\mu\mu$. In no case was a maximum found at 640 $\mu\mu$, nor has the author been able to find one recorded at this point.

One type of cell represented by No. 19, Fig. 2, has two maxima, both of about the same magnitude and very sharply defined, one in the violet at 440 $\mu\mu$, and one at 700 $\mu\mu$ or 720 $\mu\mu$. This type is obtained when, after applying the selenium to the form in the manner previously described, it is heated for about 10 hours at 180° C.

Fig. 3 shows the effect of a variation in the temperature of annealing on the shape of the wave-length sensibility curve. This set of curves is typical of a large number obtained when the conditions of temperatures were the same as those indicated here.

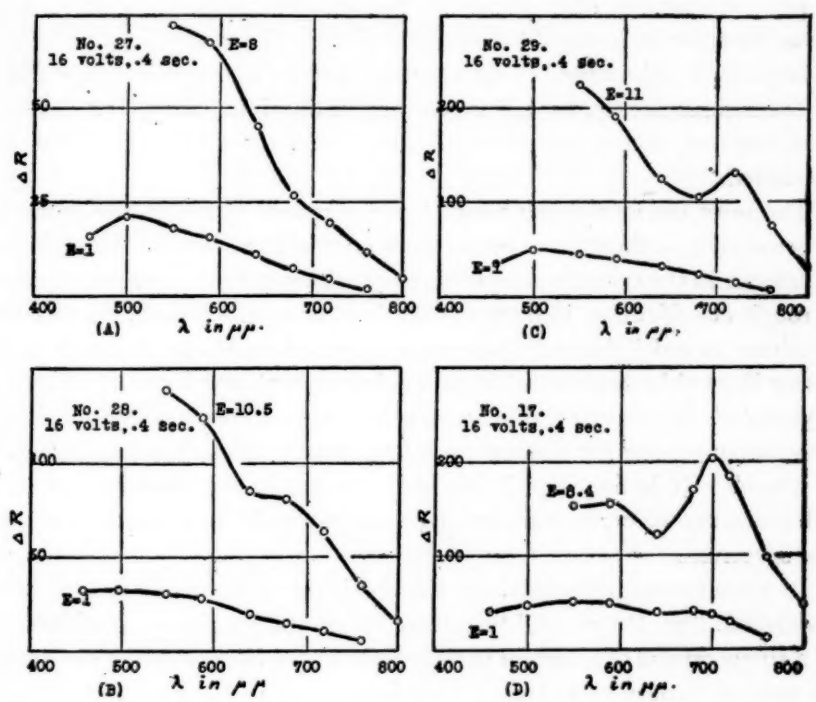

Fig. 3.

(*A*), Fig. 3, represents the type of curve obtained, when the cell, immediately after making, is subjected to a temperature of 210° C. for

some time, in this case, 4 hours. This type shows a maximum about 500 $\mu\mu$, and very little sensitiveness above 640 $\mu\mu$.

(*B*), Fig. 3, represents the type resulting when the cell on making is subjected for a short time to a temperature of 210° C., in this case 1 hour, the temperature then allowed to fall to 200° C. and kept constant at this point for 4 hours. Here is seen a change in the shape of the curve and a hint of a maximum in the red.

(*C*), Fig. 3, represents the type obtained when the cell is heated at 210° C. for 30 min., the temperature allowed to fall to 190° C. and kept constant there for 6 hours.

(*D*), Fig. 3, represents the type resulting when the cell was heated for 30 min. at 210° C. and then at an average temperature of 170° C.

The control of the maximum in the red end of the spectrum is clearly shown by the curves in Fig. 3. As the temperature of annealing becomes lower, the maximum in the red becomes, relative to that in the blue, gradually higher, until in the type (*D*) it exceeds that in the blue.

In each case described above the preliminary heating at 210° C. was given in order to lower the resistance of the cell, as was seen to be the case earlier in this paper. This was done in order to increase the accuracy of the measurements, for the apparatus for obtaining the curves is more sensitive and, hence, more accurate, the lower the resistance of the cell measured.

The most obvious explanation of the variation found in the different types of cells, in the light of recent work on selenium, rests on the probable difference in the crystals composing the various types. As we have seen, a rough classification into two general types can be made, those most sensitive to red light and those most sensitive to blue. Recently Professor Brown[1] has succeeded in producing several new forms of selenium crystals of the gray metallic variety by sublimation. A cell made by depositing one variety of these on a form was found to have a maximum at 780 $\mu\mu$. It is not improbable that the maximum sensitiveness of a cell composed of crystals of another variety should lie in the blue end of the spectrum.

In some recent investigations, the results of which have not yet been published, Drs. Brown and Sieg have found the maximum sensitiveness of a single crystal of a certain variety to be in the red end of the spectrum. In another variety two maxima were found, one in the long wave-length and one in the ultra-violet. Moreover, the location of the maximum is found to be dependent upon such factors as the angle of incidence and the intensity of the exciting light, the face of the crystal illuminated, etc.

[1] PHYS. REV., Series 2, IV, p. 85, 1914.

The explanation of the different types of cells on this basis, then, is simple. A cell, such as is represented by (*A*), Fig. 3, may be assumed to contain crystals which are sensitive to a great extent only to blue light, and few or none at all of those sensitive to red light. In other words, the temperature at which this type is annealed is too high to allow the formation of crystals sensitive to red light. Another type, (*C*), for instance, might be thought of as containing a mixture of the two varieties, the amount of the "red" crystals present not being sufficient to overcome the effect of the "blue" crystals. The type represented by cell No. 19, Fig. 2, can be explained on the same basis, *i. e.*, composed of crystals having maxima both in the red and in the ultra violet, and in which the point of maximum sensibility has been shifted towards the visible spectrum, due to a variation in some one or more of the conditions governing the formation of the crystals. The occurence of maxima separated by only a few wave-lengths can be explained by assuming a difference in the orientation of the crystals in the various cells, so that in different cells different crystal faces are exposed. Or, the light transmitted through the surface layer may suffer changes, by reflection from the crystal surfaces, causing an effect different from that it would have were it direct. This effect might be manifested by a shift in the maximum.

If the above conclusions are correct, the problem of the explanation of the light sensitiveness of selenium reduces to an explanation of the changes taking place in the single crystal under the influence of light and other agencies.

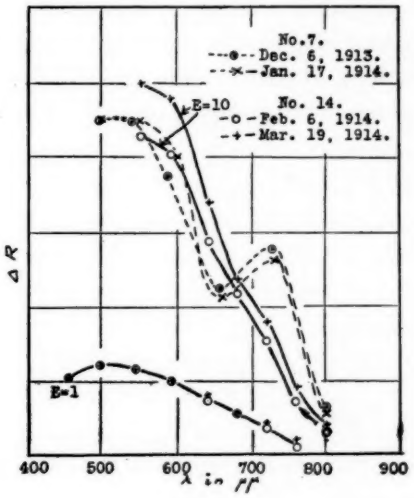

Fig. 4.

Permanence of the Characteristics.

It is evident that no definite statement as to the permanence of the characteristics of the various types can be made at the present time, since the time elapsed is hardly long enough to warrant that. Fig. 4 shows the characteristic curves of two cells taken at different time intervals, under as nearly the same conditions as possible. It is seen that they are the same in the essentials, the slight differences can be attributed to experimental errors.

SUMMARY.

In this paper has been shown:

1. That the resistance of selenium cells depends to a great degree upon the treatment to which they have been subjected while annealing them.

2. That the location of the maximum in the wave-length sensibility curve can be controlled by a variation in the conditions under which the selenium in the cell is crystallized. It was shown that the temperature variations play the most important part.

3. That the various types of cells produced in this investigation can be explained by assuming the presence of various kinds of crystals, or different positions of the same kind of crystals in the cells. The temperature at which one kind is formed may not be favorable for the formation of another kind, hence, the production of the different types of cells.

In conclusion, I wish to acknowledge my indebtedness to the staff of the department of physics for their interest in the problem, especially to Professors Brown and Sieg for the use of their apparatus, and for their many helpful suggestions, and to Messrs. Scott Walker and Paul Helmick who so ably assisted me in much of the experimental work.

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